

Review

Two-photon lithography for three-dimensional fabrication in micro/nanoscale regime: A comprehensive review

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ABSTRACT

With the advent of femtosecond lasers in the early 1990s, ultrafast laser processing has proven to be an imperative tool for micro/nano machining. Two-photon lithography (TPL) is one such unique microfabrication technique exploiting the nonlinear dependency of the polymerization rate on the irradiating light intensity to produce true three-dimensional structures with feature sizes beyond the diffraction limit. This characteristic has revolutionized laser material processing for the fabrication of micro and nanostructures. In this paper, an overview of TPL including its working principle, experimental setup, and materials is presented. Then, the effect of resolution with a focus on techniques adopted to improve the final resolution of the structures is covered. Insights to improve throughput and speed of fabrication to pave a way for industrialization of this technique are provided. Finally, TPL for microfabrication of structures with the emphasis on metamaterials is thoroughly reviewed and presented.

1. Introduction

Lithography and polymerization of photosensitive materials using light as the source for initiation of solidification is a well-established area of research in science and technology, driven by the escalating demand for smaller features and complex structures. Lasers have proven to be a powerful tool for the fabrication of complex structures in small length scales. Femtosecond laser-matter interactions first observed in the early 1990s are significantly different from the interactions of longer pulses or continuous wave lasers with the matter. When a material is exposed to a femtosecond laser beam, power density is very high, and the laser-matter interaction time is very short resulting in rapid photon energy transfer. This high transient photon fluence density induces several non-linear effects resulting in sub-diffraction feature sizes. The rapid development of such ultrafast lasers has led the way to the industrialization of laser-based systems for manufacturing and many other applications.

Additive manufacturing (AM) in the nanoscale regime is the fabrication of 3D structures that contain geometric features smaller than 1 μm in at least one dimension. Many manufacturing methods are available to produce nano-objects, but only a few are suitable for AM in the aforementioned regime. Dip-pen nanolithography (DPN) [1], electron beam lithography (EBL) [2], direct laser writing (DLW) and electro-

hydrodynamic jet printing (EHD) [3] are some of the promising techniques to obtain high resolution fabricated structures.

Direct-writing technologies are capable of manufacturing three-dimensional structures with high spatial resolution and dimensional accuracy [4,5]. Laser-based direct writing methods are especially appealing for the fabrication of 3D microstructures [6]. Among the many laser-based techniques, two-photon lithography (TPL) or also known as two-photon polymerization (TPP) is suited best for the construction of well-defined 3D micro/nanostructures because it opens the door to building structures with unmatched, high spatial resolution beyond the diffraction limit [7]. Additionally, local polymerization and sub-diffraction-limit feature sizes can be attained by employing laser beams with intensities just above the threshold for polymerization. It is unique in the sense that it enables the construction of true three-dimensional freestanding structures.

Standard photolithography, popular for the fabrication of two-dimensional structures, is based on one-photon absorption in a photo-sensitive medium. Two-photon lithography (TPL) is a ground-up and non-linear [8–11] process employed in fabricating complex, intricate 3D micro and nanostructures in which the photoresist responds to the square of the intensity and offers an enhanced resolution. Compared to the classic stereolithography (SLA) and the selective laser sintering (SLS), TPL provides superior resolution, and the process of layer-by-

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layer fabrication and recoating of wiper blades used in SLA and SLS are eliminated. One of the key aspects of TPL is its capability to produce features smaller than the point of a laser beam projected. The fundamental phenomenon on which the operation of TPL is dependent is two-photon absorption (TPA). Photopolymerization refers to the process of using light as an energy source to induce the conversion of small unsaturated molecules in the liquid state to solid macromolecules through polymerization reactions. Although other radiations, including x-ray, gamma-ray, microwave, and even electron and ion beams can induce similar curing reactions, photopolymerization deals with those that are induced by light in the UV, IR to visible spectral region. The monomers or oligomers in the liquid state upon light excitation may be solidified by two means: polymerization and crosslinking to form long chains of the polymer. Although UV stereolithography, inkjet printing and multi-jet printing are capable of producing true 3D structures, the final resolution is only in the micrometer regime. On the other hand, techniques like EBL and EHD jet printing can produce structures with resolution in tens of nanometers but are limited to only 2D structures with high aspect ratios. TPL is unique in the way that it allows true 3D fabrication of structures with superior spatial resolution. In TPL, photoinitiators are generally added to the monomer up to a few weight percents (wt%) to absorb at the wavelength of exposure and to assist the process of polymerization. Although efficient TPA has been demonstrated at different wavelengths of excitation light such as in the visible spectrum (400 nm) with effective photoinitiator absorption band in the deep-ultraviolet spectrum [12], at near-infrared wavelengths of excitation light, TPA of photoinitiators developed for absorption at wavelengths different from NIR regime are not efficient [13] and most of the commercially available resins exhibit good absorption at NIR wavelengths of excitation light. In addition, Malinauskas and coworkers experimentally demonstrated the strongest TPA phenomenon in commercially available resins when laser irradiation with a wavelength near-infrared was utilized [14]. Hence, the phenomenon of TPA is observed effectively when light with excitation wavelength near-infrared (600–1064 nm) region is employed.

In 1931, Göppert-Mayer first predicted the existence of TPA [15]. Accordingly, the SI unit for the TPA cross-section (δ) is named Göppert-Mayer (GM). However, the effect was not physically realized until the invention of lasers in 1960. Two-photon photopolymerization is based on vat polymerization (VP) and was first reported by Pao and Rentzepis in 1965 [16]. After the development of simple solid-state femtosecond lasers in the late 1980s and early 1990s, writing structures via multiphoton polymerization was first demonstrated in 1997 by Maruo et al. [17] and was widely acclaimed for its ability to fully fabricate 3D structures. However, there are several factors that influence the processing time, accuracy, and quality of the developed structures. Input power, exposure dose and the type of photopolymer play a vital role in

defining the properties and applications of the structures. The true 3D fabrication characteristic of TPL is well-suited for the fabrication of complex shapes and facilitates the construction of metamaterials. This paper emphasizes the progress in the fabrication of three-dimensional metamaterials via TPL.

2. Two-photon absorption

Photopolymerization is a photochemical reaction that takes place when photon energy is provided to a matter. Liquid materials can be converted into solid upon light exposure either through photocrosslinking or photopolymerization. Photopolymerization is the formation of polymer chains initiated by light exposure to the monomer.

The two-photon photopolymerization technique is versatile and applicable to the fabrication of many materials in the nanoscale regime. As indicated by the name, the resins are polymerized by absorbing two photons at a longer wavelength, usually in the near-infrared (NIR) spectral region. The two-photon process has mainly two advantages over single-photon absorption that is used in conventional rapid prototyping. First, most of the commercially available polymers have negligible linear absorption in the near-infrared (NIR) region, and therefore the laser beam penetrates deeply into materials and directly induces polymerization from inside without initiating any photochemical process outside of the focal volume; secondly, the quadratic dependence of polymerization rate on the light intensity enables 3D spatial resolution, and the accuracy is far better than that achieved in single-photon processes. In the process of two-photon absorption (TPA), the laser source is usually constituted of a solid-state laser (Ti-sapphire) and an ultrashort pulse-width of less than 100 fs oscillator operating at a wavelength near-infrared regime (~ 800 nm) to obtain sufficient peak intensity at a low average laser power. However, nowadays second harmonic fiber lasers are being used extensively as they are more affordable and reliable and operate at ~ 780 nm [18]. This controlled laser beam is tightly focused onto a photocurable resin through a high numerical aperture (NA) objective lens, which consequently creates photo density profiles with an equal number of photons at all cross sections on the focused spot. The resin is exposed only within the focal volume of the beam generally known as voxel [19] and the process of two-photon polymerization (TPP) is restricted only to this volume giving rise to a 3D resolution. A high numerical aperture objective lens is used for closely focusing the laser onto the resin, which enables achieving a high photon density near the focal point to fabricate sub 100 nm structures. In 3D micro-fabrication, the voxel size is proportional to $\frac{1}{(NA)^4}$. Thus, a large NA value is crucial for superior resolution. Generally, $NA \sim 1.4$ is utilized in the case of oil-immersion lenses for realizing high fabrication resolution. Although the resolution of the TPL technique is generally related to sub-

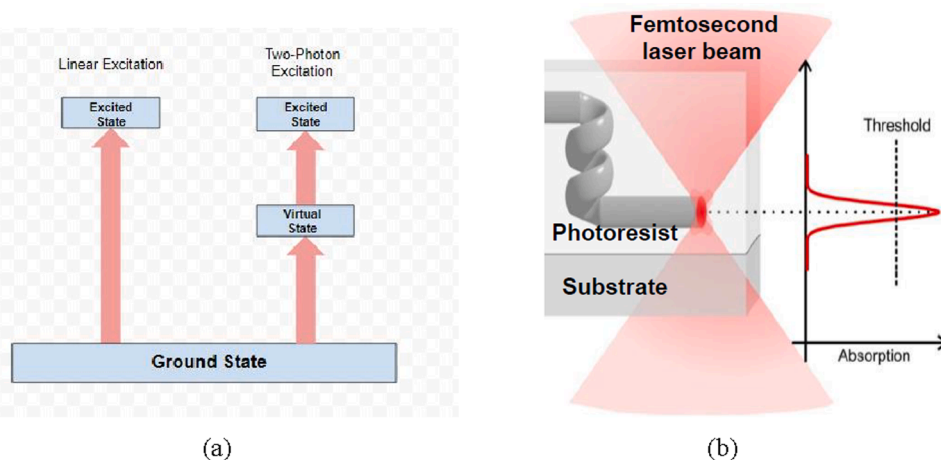


Fig. 1. (a) Schematic of non-linear absorption. (b) depiction of the laser intensity distribution during two-photon absorption [22].

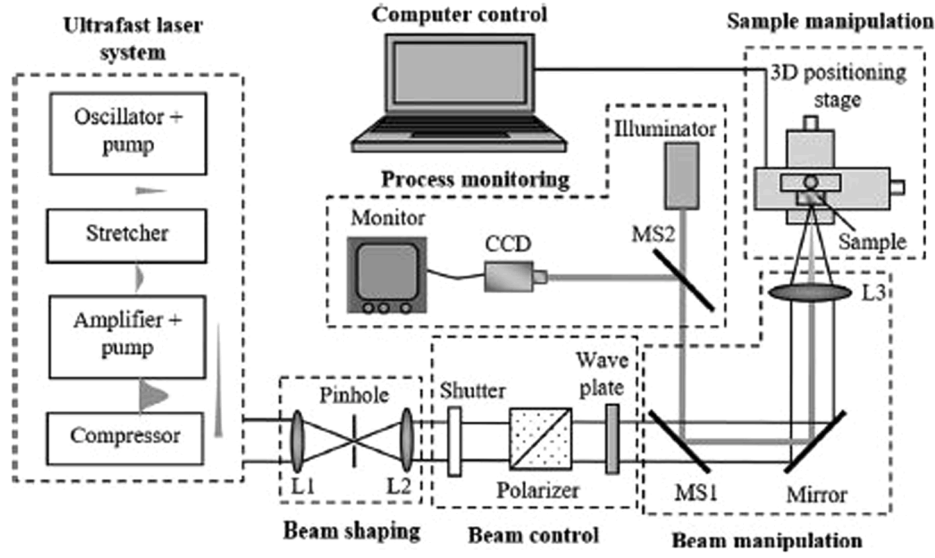


Fig. 2. Schematic of two-photon polymerization setup [23].

wavelength, its axial and lateral resolution are still fundamentally governed by Abbe's Law, which states that the resolution of an optical microscope is inversely dependent on its aperture [20]. The major advantage of this technique is that outside the region of the focal point, the incident light is below the exposure threshold of the photosensitive medium and can pass through it with no photo-chemical reaction evident beyond the voxel.

Zhou et al. [21] presented a theoretical relationship between the voxel diameter and the density of radicals.

$$d(P, t) = \omega_0 \cdot \left(\ln \frac{\sigma_2 I_0^2 n \tau}{c} \right)^{1/2} \quad (1)$$

where d is the voxel diameter as a function of input laser power, P , and total irradiation time, t . ω_0 is the beam waist, σ_2 is the effective two-photon absorption cross-section, I_0 is the photon flux at the point of maximum intensity, τ is the laser pulse width, n is the number of pulses and c is defined below as

$$c = \ln \left[\frac{\rho_0}{\rho_0 - \rho_{th}} \right] \quad (2)$$

where ρ_0 is the density of free radicals at the focal plane and ρ_{th} is the threshold density of free radicals. Similarly, the axial length of the voxel is described as

$$l(P, t) = 2z_R \cdot \left(\left(\ln \frac{\sigma_2 I_0^2 n \tau}{c} \right)^{1/2} - 1 \right)^{1/2} \quad (3)$$

where z_R is the Rayleigh length given by

$$z_R = \frac{\pi \omega_0^2}{\lambda} \quad (4)$$

The ability of the resin to absorb two photons simultaneously, which assists the laser beam in bypassing the usual diffraction limit, plays a major role in this technique. Fig. 1(a) illustrates the process of two-photon excitation upon light irradiation. TPA can transpire through two excitation processes, namely, sequential excitation and simultaneous two-photon excitation. In sequential excitation, a photon is absorbed by the electrons, which leads to a real intermediate state being populated by these electrons with a well-defined lifetime of 10^{-4} to 10^{-9} s. From these electrons, a small population goes on to absorb the second photon in order to complete the process of TPA while the majority of them emit energy and return to their ground state. In contrast, the

second process (simultaneous excitation) does not involve any such intermediate state. A virtual state is created when the electrons interact with the first photon and the second photon is absorbed if and only if it approaches within the virtual state lifetime given as 10^{-15} s in order to complete the process of TPA. To achieve this, a high intensity laser source is essential.

For DLW via simultaneous two-photon absorption, a high-powered femtosecond pulsed laser generated from a mode-locked Ti:Sapphire oscillator or any other MHz-rate oscillator is usually utilized because of its high bandwidth. Fig. 2 shows a typical femtosecond laser setup for TPL. In principle, by optimizing the exciting laser wavelength to assist nonlinear absorption, structures can be fabricated at the same rate as the repetition rate of the laser. Some of the parameters best suited for TPL are average input laser power of several milliwatts – 10 W, repetition rate of 1 kHz – 100 MHz, and central wavelength of 515 nm – 1064 nm depending on applications. Several other optical elements such as beam isolator (Faraday isolator) and shutter are used in combination to prevent back reflection and as an obstruction for the beam when not in use. An acoustic optical modulator can also be used as a shutter. Additionally, a beam splitter can be utilized for polarization and spectroscopy. Step size and dwell time are important parameters that define the resolution, feature size, accuracy, and uniformity of the patterned structure. The laser input power can be manipulated by a variable attenuator comprised of a half-wave plate and a polarizer. A beam expander can be utilized to illuminate the back aperture of the objective completely. Generally, for enhanced resolution, high numerical aperture objective lenses are used. Depending upon the application, dry lens or oil immersion lenses are utilized. When immersion fluid is used to obtain high NA and enhanced resolution, glass is usually used as the substrate because glass and the photoresist have almost the same index of refraction. For metamaterial applications, particularly terahertz frequencies, a silicon substrate with a high resistivity is utilized and dry lenses with high NA (0.90–0.95) are used due to the significant difference between the refractive indices. A CCD camera at the back of the objective allows monitoring of the process while running. 3D stages with high precision and resolution can be employed for 3D scanning of the laser beam relative to the sample movement. Improved scanning speed can be achieved via two-dimensional galvanometer scanners integrated with a one-dimensional piezoelectric stage. With the advent of digital micromirror devices (DMDs), micro-lens arrays (MLAs), spatial light modulators (SLMs), and high precision 3D linear motor stage, fabrication of microstructures over large areas, replication of structures with high speed and accuracy has become a reality.

In DLW or TPL, pulsed femtosecond lasers are used, and the spatial bell-shaped Gaussian distribution is well suited for the electric field strength, E (V/m), fluence, F (J/cm²), intensity, I (J/cm²), and exposure dose, D (J.s/cm²).

$$E(r) = E_0 \exp\left(-\frac{2r^2}{r_0^2}\right) \quad (5)$$

$$F = \frac{2E(r)}{\pi r_0^2} \quad (6)$$

where r_0 is the beam waist, and r is the radius of the beam.

Generally, TPL requires a thin glass slide, a lens and immersion oil (to increase the resolving power of the microscope) that helps the laser beam to strictly focus to a fine point. However, one of the major drawbacks of TPL is its limitation in throughput caused by seriality. This makes it cumbersome and time-consuming to pattern large areas or to produce multiple structures simultaneously. Some of the alternatives for such limitations are optical holography or interference lithography [24], or TPL with optical masks [25–27].

It is noteworthy that the viscosity of the system plays a significant role in influencing the reaction kinetics. The Stokes-Einstein and Smoluchowski equation links the dependence of the diffusion coefficient with the viscosity [28].

$$k_d = \frac{8000 \times R \times T}{3 \times \eta} \quad (7)$$

where k_d is the diffusion coefficient (dm³/mol/s), R is the universal gas constant (J.K/mol), T is the temperature of the system (K), and η is the viscosity (Pa.s). From the above equation, the greater the viscosity of the system is, the faster the polymerization process is. However, this relationship is valid only when the viscosity of the system is not extremely low or high. Initially, if the viscosity is too high, then the propagation of the polymerization is diffusion-limited and if it is too low there is a chance of the structure floating to the top. Mechanical failures can also occur during the development when the liquid cohesive forces are greater than the restoring forces of the polymer [29]. The cohesive forces emerge due to the decreasing level of resin, which forms a concave meniscus between the features of the polymerized structure. These forces can cause the bowing of some parts because of the scaling effects of surface tension forces in the microscale. These effects can be overcome by making the walls of the fabricated structure thicker and stronger. However, the fabrication time is increased, and post-processing of the structure is required to obtain accurate dimensions. An alternative technique is to perform rinsing using supercritical CO₂ drying [30]. This method is widely used as the surface tension effects are almost eliminated because supercritical fluids have properties similar to both gases and liquids, thus eliminating gas-liquid interfacial effects.

3. Materials

Most of the materials used for TPL are readily available, standard materials, which are applicable to conventional lithographic processes. Photoresists or photocurable resins are largely made up of two components: photo-initiators (radical polymerization) or a photoacid generator (PAG) (cationic polymerization) and a monomer. An optional inhibitor may be utilized, which assists in the termination of the polymerization process. A material whose solubility decreases on exposure to light is called a negative-tone photoresist [31]. In the two-photon polymerization (TPP) process, free radicals are generated through light exposure onto a photo-initiator, followed by the cross-linking of the monomers/oligomers to form long polymer chains. The polymerization eventually terminates via interference of radicalized monomer with active species, or interference with radicalized monomers or via depletion of monomers as a consequence of the action of inhibitors. On the other hand, with positive-tone photoresists, TPA breaks down the polymeric chains and

makes them soluble. Hence inverse structures are written. In general, TPP is applied to radical polymerization where the active species react with the monomers to form high molecular weight materials. The rate of polymerization via radical mechanism is high for acrylate-based monomers [32,33], which helps in reducing process times. Resins utilized for TPL must possess certain characteristics such as transparency in the visible and near IR frequency regime to allow laser pulses penetrate deep into a region inside the resin without any single-photon excitation. The resin must attain fast curing speed and the polymerization must be confined to the focal spot with negligible scattering [34]. High viscosity, high glass transition temperature post-curing, and resistance to shrinkage are some of the properties of a suitable resin for TPL application. Shrinkage is a common disadvantage associated with polymers due to the change in density before and after curing. It is necessary to pre-compensate for this effect to obtain a well-defined 3D structure [35]. The most popular materials in the case of two-photon lithography are acrylate- and epoxy-based resins because of their high optical transparency and applications.

SU8 is one of the most widely used commercialized photoresists [10,33,36–38] because of its availability and suitable properties for the TPL technique. One of the unique properties of SU8 is its two-step cross-linking process. Firstly, a strong acid is established during the exposure, which is secondly followed by an acid-initiated, thermally driven epoxy cross-linking during the post-bake process [39]. The possibility of 3D fabrication of SU8 via TPL was first demonstrated by Witzgall's group in 1998 [10]. They employed single shots of laser pulses from a femtosecond amplifier for the fabrication of small three-dimensional dots via TPL. More complex 2D and 3D structures were later fabricated by various groups incorporating various photo-initiators and novel methods of fabrication. High aspect ratios in the range of 50:1 have also been achieved by Teh et al. [36] using low numerical aperture optics on the SU8 photoresist. SU8 can also be combined with various other mixtures/dyes to obtain functional properties and for in-situ applications [40]. SU8 being a negative-tone photoresist leaves behind a well-defined 3D structure once it is exposed to the laser beam while the unexposed portion is generally soluble in developing solutions. Because of its unique optical properties, SU8 has been considered as a feasible and effective polymer for the fabrication of photonic crystals and metamaterials. Although the resolution that can be attained with SU-8 via TPL is poor compared to those with some radical systems, SU-8 is thermally stable, transparent in the visible spectrum and attains high resistance to solvents, making it highly suitable for these applications.

Other materials like hydrogels have been extensively used for diverse applications in the field of tissue engineering and drug delivery [41–44]. Lucirin® TPO-L, Irgacure®-369, Irgacure®-184 are some of the photo-initiators largely used for radical polymerization in TPL methods because of their price and availability. Rose Bengal is also a common water-soluble photoinitiator suitable for TPL at 800 nm. Among the above-mentioned photo-initiators, Lucirin® TPO-L is found to be better due to its availability in solid and liquid form, making it suitable for high loading and its easily soluble property in most of the commercially available resins [45]. Although the two-photon absorption coefficient and the TPA cross-sections are very small compared to IR absorbing dyes, the fabricated structures using Lucirin® TPO-L as the photo-initiator have exhibited superior resolution at low laser power, resulting in a quantum yield of 0.99 [46]. Functionalizing polymers by incorporating other materials for specific applications has also been demonstrated [47,48].

TPL of three-dimensional microstructures using non-photosensitized polymers, organic-inorganic hybrids and ceramics have also been pursued by various groups [49–52]. Additionally, organic/inorganic photosensitive material with a higher concentration of inorganic content can be utilized to fabricate inorganic 3D photonic crystal structures by TPL with appropriate thermal post-treatment. ORMOCER® is one such silicate-based photopolymer, which allows the fabrication of high-resolution 3D structures with enhanced mechanical properties and

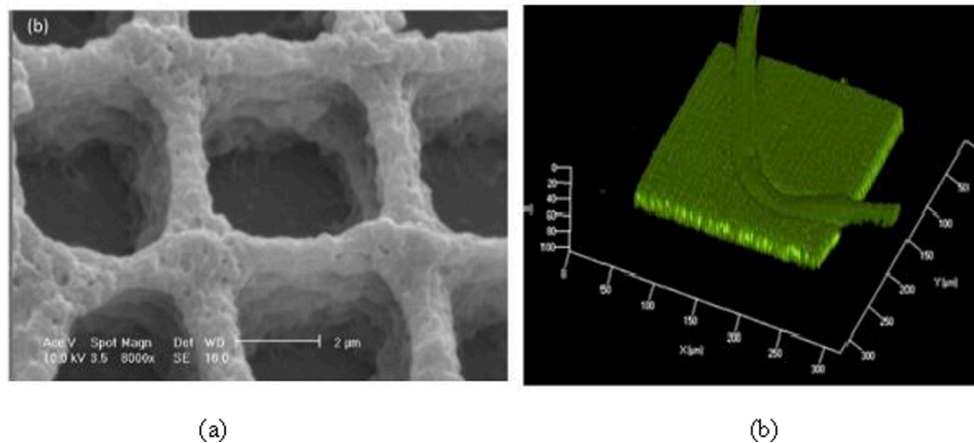


Fig. 3. (a) Bovine serum albumin (BSA) structure. (b) Photopolymerized BSA capturing a live C-elegans worm [57].

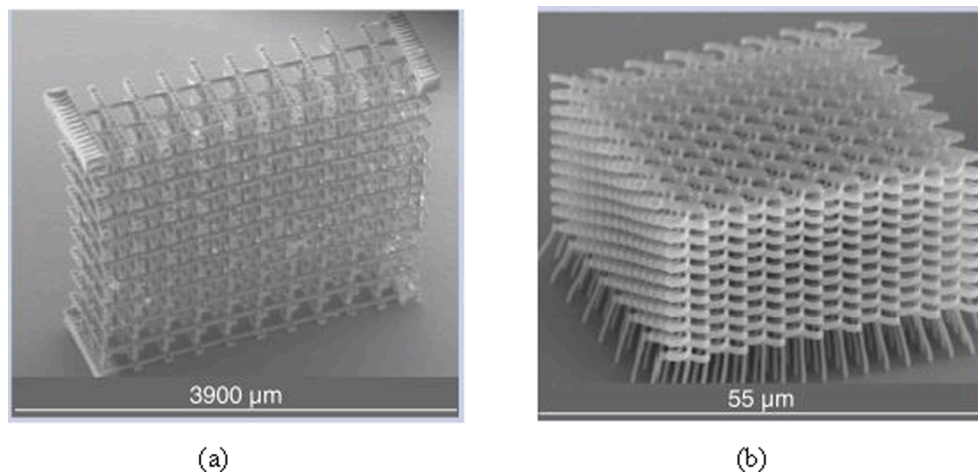


Fig. 4. (a) 3D scaffold for tissue engineering. (b) 3D helix-based photonic crystal structure template [55].

fine-tunable optical properties for photonic applications with optical bandgaps. Hybrid polymers provide more flexibility in design and impart enhanced mechanical properties to the structure, which are the main aspects in drug delivery and tissue engineering applications. Ovsianikov et al. [50] developed microneedles via two-photon polymerization technique for drug delivery and other biomedical applications utilizing ceramic-polymer hybrid material for enhanced mechanical properties and greater aspect ratio. Similarly, Emons' group [53] utilized a zirconium-based inorganic-organic hybrid polymer producing structures with a 45 nm resolution and high structural

stability.

Proteins and metals are materials other than polymers, which have been utilized in a broad variety of applications for TPL. Inexpensive proteins like bovine serum albumin (BSA), fibrogen and collagen have been used to fabricate single/multi-storey scaffolds for cell growth and tissue engineering [54,55]. Fig. 3 shows a simple 3D BSA scaffold for the assessment of compatibility and stability of the structure to entrap and grow enzymes and microbes. Fig. 4 depicts the difference in size (~70 times) between a 3D scaffold for tissue engineering and a 3D photonic crystal. TPL has great potential for the construction of tailored and

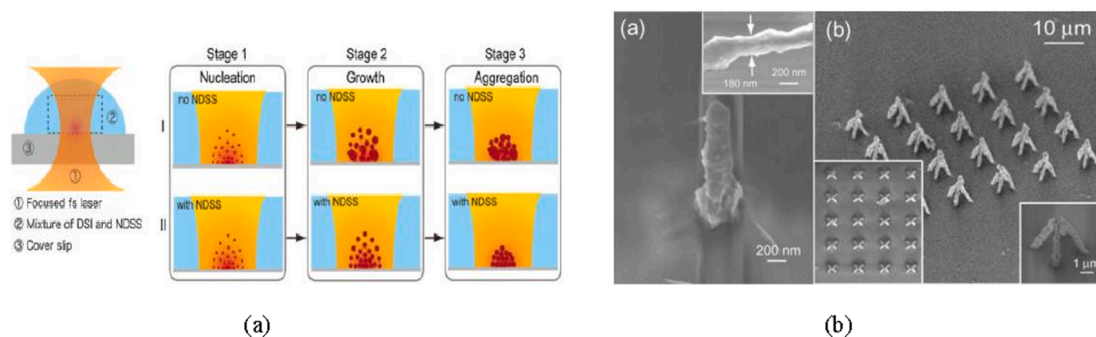


Fig. 5. (a) Schematic illustration of the formation of silver stripe patterns through the multiphoton-induced reduction process. In the absence of NDSS, varized particles with different shapes are formed, whereas particles with uniform size and shape are created by adding NDSS. (b) free-standing 3D silver pyramids on a substrate. From [59].

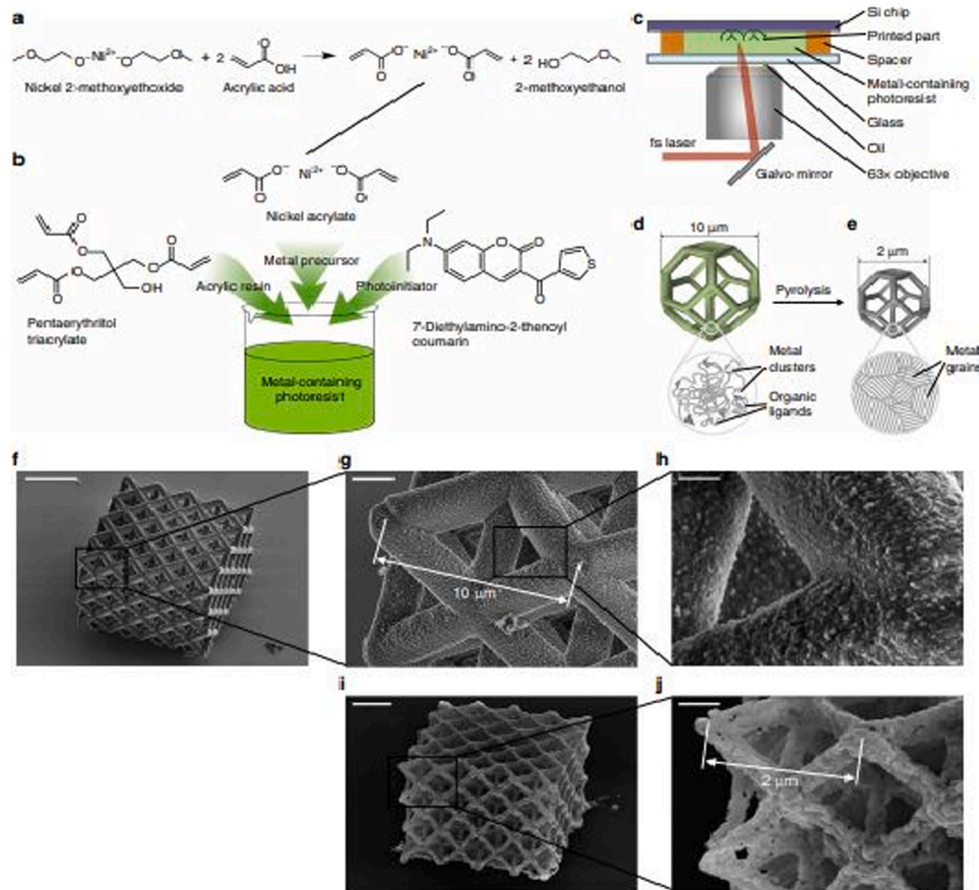


Fig. 6. (a) Reaction synthesis of the metal precursor. (b) metal precursor, acrylate-resin and photoinitiator mixed to form the photoresist. (c) Schematic of TPL process. (d-e) fabrication and pyrolysis. (f-h) SEM images of the octet nanolattice. (i-j) representative nickel nanolattice. From [69].

functional biostructures in the micro/nanoscale. However, the major drawbacks of using proteins or hydrogels are: i) the mechanical properties of cross-linked proteins are poor, which limits the structural design, ii) low viscosity of aqueous photoresists limits the complexity of the structure, and iii) high photosensitivity of proteins can give rise to structural distortions and inhomogeneity. A detailed review of the advantages, disadvantages, and applications of various commercial and customized photoresists can be found in ref. [56].

Metals are of paramount importance in the fabrication of electromagnetic, photonic metamaterials to realize supernatural effects, viz., invisibility cloaking and superlensing. Additionally, metals are predominant in micro/nanoelectronic applications. Since the inception of microchips, researchers have been continually investigating several techniques to achieve metallic structures in the nanoscale regime. Ishikawa and co-researchers [58] proposed one such novel fabrication procedure based on two-photon induced reduction of metal ions for 3D micro/nanostructures. A femtosecond laser beam was tightly focused onto metal complex ions, which were photo-reduced to metal nanoparticles by simultaneous absorption of two photons. Feature sizes in the range of few tens of micrometers were achieved. Metals are of supreme importance in plasmonic and metamaterial applications. Since the feature sizes for plasmonic applications are in the range of few hundreds of nanometers or even smaller, the major hindrance for superior resolution is the unwanted crystal growth during irradiation. Cao and co-workers [59] overcame this problem by introducing a dopant surfactant molecule as a crystal growth inhibitor. As shown in Fig. 5, particles with uniform size and shape were obtained by employing a crystal growth inhibitor. The feature size achieved was ~ 180 nm for 3D nanostructure and ~ 120 nm for 2D silver patterns on the substrate. TPL integrated with other technologies like laser-induced forward/backward transfer

(LIT) can also produce nanodroplets with superior resolution and enhanced mechanical and optical properties for metamaterial and plasmonic applications [60].

Formanek and colleagues [61], in their experiment, demonstrated 3D metallic-polymer periodic structures spread out over a large area for microelectronics and metamaterial applications. Initially, a large number of 3D polymer structures were fabricated in parallel using multi-lens array and regenerative amplifiers for the laser beam. Subsequently, the substrate was coated for hydrophobic action and the polymer structures were pre-treated with SnCl_2 . Finally, a selective silver overcoating solely on the polymer structures was realized in producing more than 700 components. In 2000, Wu's group [62] demonstrated two-photon photographic production of 3D metallic structures within a dielectric matrix. The three-step procedure included the use of sol-gel, metal aqueous solution matrix and TPL for the creation of the latent image. This was followed by two-photon exposure for the development of the image into a 3D structure and finally a post-treatment and fixing step to produce 3D metallic structures. Similarly, Shukla et al. [63] presented a novel method for producing metallic nanostructures with sub-wavelength resolution using TPL in a polymer matrix. They employed in-situ initiated reduction of metal salt and simultaneous polymerization of the negative-tone photoresist via two-photon absorption within a photoresist film. Uniform gold nanoparticles as small as ~ 10 nm were achieved via two-photon writing in gold precursor doped photoresist. Tosa et al. [64] also demonstrated the fabrication of metallic nanowires via simultaneous photoreduction and polymerization through TPA. According to their experiment, an iron (III) citrate complex acting as a photo initiator, upon excitation, generated iron (II) citrate that reacts with the metallic cations producing metals. To maintain homogeneity in the dispersion and avoid precipitation of metallic salt within the solution

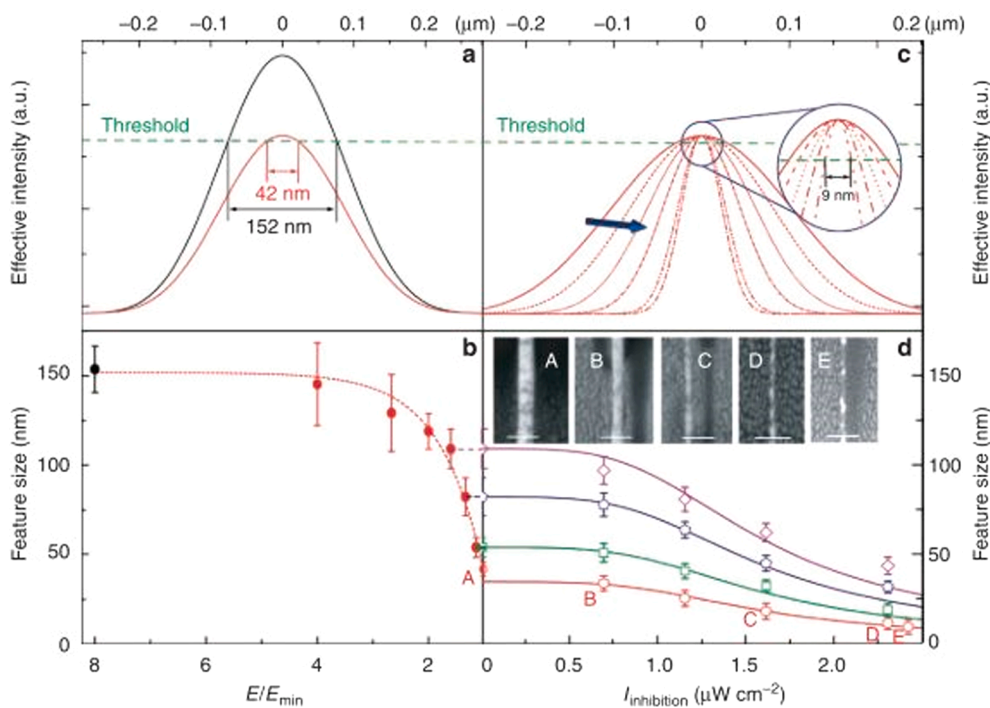


Fig. 7. Schematic demonstration of the feature size reduction in TPL by decreasing the writing laser beam energy dose to the polymerization threshold of the resin. (a) single beam approach. (b) feature size vs writing laser beam energy dose without inhibition beam. (c) schematic illustration of feature size reduction in the two-beam approach by increasing the intensity of the inhibition beam. (d) feature sizes of free-standing lines versus the intensity of the inhibition beam, under the exposure of writing beam with different energy doses. From [70].

before the exposure, the water-soluble polymer was utilized. One key advantage of polymer-metal or polymer-ceramic processing is obtaining, in bulk, the strengthening effects associated with the material in thin film form factor [65]. The thickness of the obtained structures in the nanometer regime and the construction of templates with resolution in a few tens of nanometers are currently viable only through two-photon lithography.

In 2006, Tanaka et al. [66] employed TPL for the fabrication of 3D metallic, electrically conductive nanostructures. In their study, it was found that the metallic nanostructures were highly electrically conductive and had low resistivity values unlike the structures obtained by Stellacci et al. [67] via laser and electron beam induced growth of metal nanoparticles inside a polymer. Similarly, Nakamura et al. [68] conducted elemental analysis and measurement of electrical performances of 3D silver structures fabricated via TPL and simultaneous reduction of the metal. The results comply with the results obtained by Tanaka et al. [66]. Recently, Vyatskikh and colleagues [69] developed a TPL based technique to fabricate 3D nano-architected metals with ~ 100 nm resolution. This breakthrough was achieved by first synthesizing a hybrid-organic-inorganic material constituting nickel (Ni) clusters producing a metal-rich photoresist as shown in Fig. 6. Subsequently, the photoresist, after the polymerization process, underwent pyrolysis to eliminate the organic component producing a greater than 90% in wt Ni containing 3D structure. Nanolattices such as octet architecture were fabricated employing this method, which proves to be an imperative factor in the fabrication of optical and mechanical metamaterials. The main advantage of this technique lies in the ease of process without compromising the resolution.

However, beyond the melting point of the metal during laser irradiation, sudden unwanted growth, ablation effects, or a drastic change in the absorption coefficient of the metal can degrade the controllability of fabrication attributes such as resolution and the shape of the pattern being written by the TPL technique. Therefore, for metamaterial applications, a polymer template is usually first fabricated via TPL and then coated with metal nanoparticles using appropriate techniques. The continuous metallic film could be deposited on the surface of the polymer lattice through either electroless plating, atomic layer deposition (ALD), sputtering or electroplating, and subsequently the template could

be removed by dissolving or chemical etching.

4. Resolution

The minimum lateral and axial distance at which two adjacent features can be distinctly patterned without any overlap is defined as the writing resolution. The nonlinear absorption behavior exhibited during two-photon lithography extends the possibility to exceed the diffraction limit and fabricate features with sub-diffraction limited resolution. In 2001, Kawata et al. [7] demonstrated the minimum resolution of 120 nm with fine feature size achieved via TPL. Since then, for a long time, researchers have been attempting to obtain sub 100 nm feature sizes and resolution. In 2013, Gan et al. [70] reported a feature size of 9 nm and 52 nm two-line resolution achieved via TPL by tweaking certain parameters viz. exposure dose, input laser power, inhibition laser power. In addition, this is one of the smallest feature sizes obtained via TPL in the published literature. As shown in Fig. 7, laser power, exposure dose and concentration of active species in the voxel after absorption are vital parameters characterizing the writing resolution, linewidth and feature size of the structure. Appropriate optimization of these parameters results in superior resolution. The voxel volume varies directly with the cube of the wavelength of the light source. This implies smaller the wavelength, the smaller the voxel dimensions become. Schwarz et al. [71] demonstrated that the developed linewidth and resolution were much superior for a TPL fabrication when compared to one photon exposure. However, in practice, the concentration of active species in near surroundings of the voxel increases with exposure due to the presence of residual active species. This effect produces undesirable polymerization surrounding the voxel, resulting in thick lines and adversely affected spatial resolution. Scanning speed also plays a vital role in defining the resolution of fabricated structures. At certain laser power, the resolution has a linear relationship with the scanning speed, i.e., higher scanning speeds result in enhanced resolution. This is due to the fact that exposure dose is reduced, leading to the reduction in linewidth. However, very high scan speeds can hinder the process of polymerization and result in weaker and easily collapsible structures. Therefore, optimum selection of input laser power and scanning speed is essential for TPL.

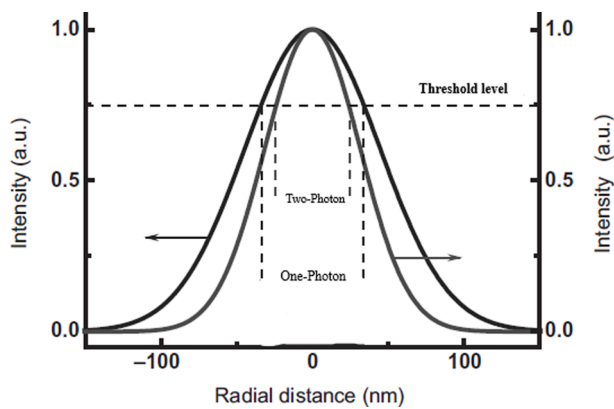


Fig. 8. Comparison between light intensity profiles generated by one-photon and two-photon absorption for same conditions [65].

In TPA, the absorption of photons depends on the square of the intensity of the light source, resulting in the profile of exposure dose in TPL being different than the focal light intensity profile in the case of one-photon absorption. The radius of the profile of the exposure dose coincides with that of the laser light intensity volume, but the full width at half maximum is narrower by a factor of $\sqrt{2}$ as shown in Fig. 8 [65,71]. Another parameter that is critical to the final resolution is the numerical aperture (NA) of the objective. The highest angle between two propagating waves from diametrically opposite ends of the aperture corresponds to the highest spatial frequency fringes and consequently determines the resolution of the objective. The NA of an objective is defined as $NA = n \sin(\alpha)$, where n is the refractive index and α is the maximum angle measured from the outer edge of the objective lens with respect to the optical axis. The resolving power of an objective varies and scales laterally as the inverse of its NA and axially as the inverse of the square of the NA, and therefore high NA objective lenses are used for TPL techniques to obtain superior resolution. However, due to the residual effect, the spatial resolution obtained is always greater than the size of an isolated structure such as a dot or a line, generally called linewidth and is in the order of ~ 150 nm [72]. The same is true in the axial direction considering the fact that feature size in the z-direction is much larger. In photopolymerization, for a given polymerizable group, low curing speed indicates low quantum yields. An increase in the photosensitivity of the resin, where the photosensitivity can be expressed as the amount of photo energy that is required to react with a half of the monomers, can increase the quantum yield of the photoinduction and photopolymerization triggered by the photons absorbed.

Invariably, the population density of photons required to reach the polymerization threshold is reduced, which potentially leads to a reduced light scattering. As a result, the polymerization caused by the detrimental factor is minimized leading to a smaller polymerization voxel.

One particular approach to this issue is to use multiple beams of laser light for the initiation and inhibition of polymerization. Testa et al. [73] demonstrated this concept by employing reversibly switchable fluorescent proteins for optically switching the molecules in the near surroundings of the voxel to a more stable energy state in order to negate the residual effects. Unlike the initiation beam, which is generally a Gaussian beam having a high intensity point, the inhibition beam is flat and exhibits no such high intensity point. Fig. 9 shows the feature sizes in the order of 40 nm or $\sim 1/12$ th of the wavelength of irradiated light achieved by Cao's group [74] by employing an inhibition light working in the continuous wave mode simultaneously with high photosensitivity resins. Theoretically, the size of the writing beam can be pushed to zero by increasing the power intensity of the inhibition beam which consequently enlarges the volume of photo-inhibition and therefore confining the voxel to a very small value. However, due to the presence of several other non-linear effects, irreversibility of the depletion of concentration of photo-initiators and the increase in the volume of photo-inhibition, it results in decreased linewidth only. The spatial resolution remains the same or is even increased.

Lee et al. [75] proposed a minimum power and minimum exposure time scheme (MPMT) for small and low aspect ratio voxels incorporating radical quenchers and post-processing techniques, which resulted in a resolution of the order of 60 nm. Stimulated emission depletion microscopy (STED) is another technique like the reversibly switchable concept, except that the power of the inhibition beam is high to completely deplete the species concentration in the vicinity of the voxel. In STED, the molecules are excited to a higher energy state via TPA. Specifically, a Laguerre-Gaussian mode is employed, which attains a

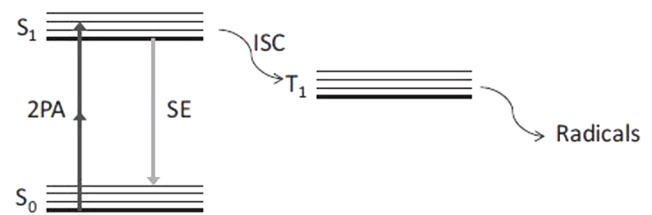


Fig. 10. Schematic of photophysical reactions occurring in a STED process. From [65].

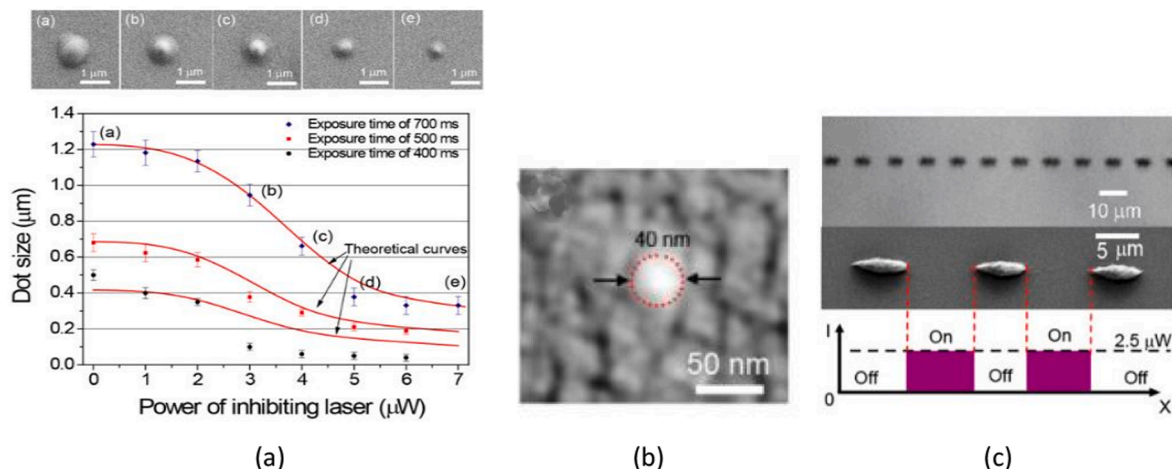


Fig. 9. (a) dot sizes plotted as a function of the power of inhibition laser in the BPE-100 photo-resin. (b) SEM image of the dot of 40 nm feature size. (c) SEM images of the dashed lines fabricated in BPE-100 photo-resin by irradiation of inhibition beam at regular time intervals. From [74].

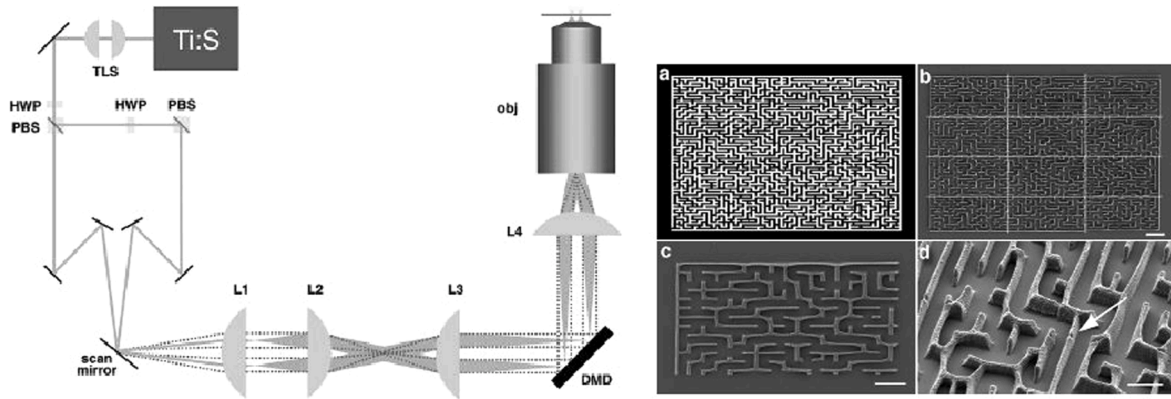


Fig. 11. (a) Schematic of multifocal multiphoton lithography setup with two independent beams generating distinct focal spots. (b) (top left) BSA-based maze split into 12 sequentially scanned masks with four rows and three columns. (top right) SEM image of the BSA-based maze. (bottom left) SEM image of one unit of the 12 sections. (bottom right) magnified image of the maze. [87]

ring-like profile inhibiting the photo-initiator molecules in the circular vicinity of the voxel. In principle, the molecules return to the ground state via fluorescent emission. However, in TPL, as shown in Fig. 10, this state undergoes an intersystem crossing (ISC) process to form a triplet state, which aids in further generating radicals that promote the process of polymerization. The downside is that there are only a few radical photo-initiators that satisfy the conditions for this technique. Hell et al. [76] demonstrated a new type of scanning fluorescence microscopy overcoming Abbe's diffraction limit by employing STED to inhibit the fluorescence process. They claim to have achieved an enhanced resolution by a factor of 4.5. Similarly, Fischer et al. [77] demonstrated improved spatial resolution in the lateral and axial directions during the fabrication of 3D woodpile photonic crystals using STED microscopy with direct laser writing. A continuous wave laser at 532 nm was utilized as the inhibition beam with a custom-made mask to generate spherical exposure volume. For a typical STED setup, the diameter of the exposure is given by the formula [23].

$$d \approx \frac{\lambda}{2NA \times \sqrt{1 + \frac{bI_{STED}}{I}}} \quad (8)$$

where NA is the numerical aperture of the objective, I_{STED} is the intensity of depletion light, I is the switching intensity at which a half of the radicals will be depleted through stimulated emission, b is the coefficient dependent on the shape of the beam, and λ is the wavelength of irradiating light.

Photo-inhibited super-resolution (PInSR) lithography is another strategy developed to achieve improved resolution. Unlike STED, in PInSR, an inhibition laser beam is used to generate radical traps from the inhibition molecules previously added to the resin. These traps react with the polymer chain to terminate the polymerization process [70,78]. Diffusion of radical quenchers in the resin is another technique for improved feature size and resolution. In this method, the quencher molecules are added to the resin before polymerization, which alter the polymerization threshold in the voxel as well as in the vicinity due to diffusion during the photo irradiation [79]. The resolution achieved with this method is comparable to the STED approach for similar structures, and interestingly the linewidth is also reduced. The main advantage of this strategy is that use of inhibition laser is eliminated. Although the results of all these techniques are extremely impressive, the smallest linewidth and resolution obtained to date are for discontinuous fabrications (dots). Moreover, the reproducibility at an extremely high resolution is poor due to high sensitivity to fluctuating input powers. Hence, there is a lack of evidence for true nanometer resolution. However, incorporating some of these techniques into the TPL process can bring out the full potential of this technique in the field of nanomanufacturing.

5. Advancements in two-photon lithography

With the advent of highly efficient photo-initiators, optical systems and laser technology, two-photon lithography (TPL) has been recognized as an effective manufacturing technique in the micro and nano-scale regime. However, TPL takes a relatively long time to fabricate structures due to seriality. Malinauskas and coworkers [80] have expressed the approximate time required to fabricate 3D structures by the equation given below.

$$t = \frac{xyzF}{R\nu} \quad (9)$$

where t is the processing time in seconds, x, y, z are the dimensions of the structure in μm , F is the fill factor which lies between 0 and 1 (ratio of polymerized to the non-polymerized volume), R is the structuring resolution or the area of cross-section of the voxel in μm^2 , which depends on the input laser power and the NA of the objective used, and ν is the scan velocity in $\mu\text{m/s}$.

For TPL to be considered as a viable option for mass-production, high-throughput, repeatability, traversing speed and capacity are the crucial factors to be addressed. Photo-initiators and resins with large dynamic range allow the user to vary the input laser power, and consequently the scan speed. However, Kawata et al. [81] demonstrated varying aspect ratios for different laser powers and exposure times while keeping their product constant. Custom-made photo-initiators with large absorption cross-sections and high dynamic range have proven to increase the speed of the polymerization process [82,83]. Nevertheless, these photo-initiators are time-consuming and difficult to synthesize. Li et al. [84] produced a custom-made photo-initiator, which is simple to synthesize, has a wide dynamic range and has a moderate area of absorption cross-section. Another parameter that can alter the process of polymerization is the frequency rates of the pulses from the oscillator. Kilohertz frequencies are well-suited for the polymerization process to be dominated by two-photon absorption and not by any other photo-thermal processes. Interestingly, many research groups [49,85] have noticed that low repetition rates, less than 1 MHz, enable high resolution patterning. This is assumed to be due to the fact that the time for diffusion of heat is higher and the accumulation of heat and hotspot creation is reduced.

As discussed earlier, utilization of galvo mirrors, digital mirror devices (DMDs), or multi-lens array (MLAs) is some engineering technique to improve the fabrication speed and throughput. Galvo scanners consist of a pair of mirrors attached to the motors that rotate them at high speeds within a certain range of angular distance. Usually, the vector scan approach implemented for TPL with galvo mirrors tends to be quicker than the raster scan approach. On the other hand, a digital

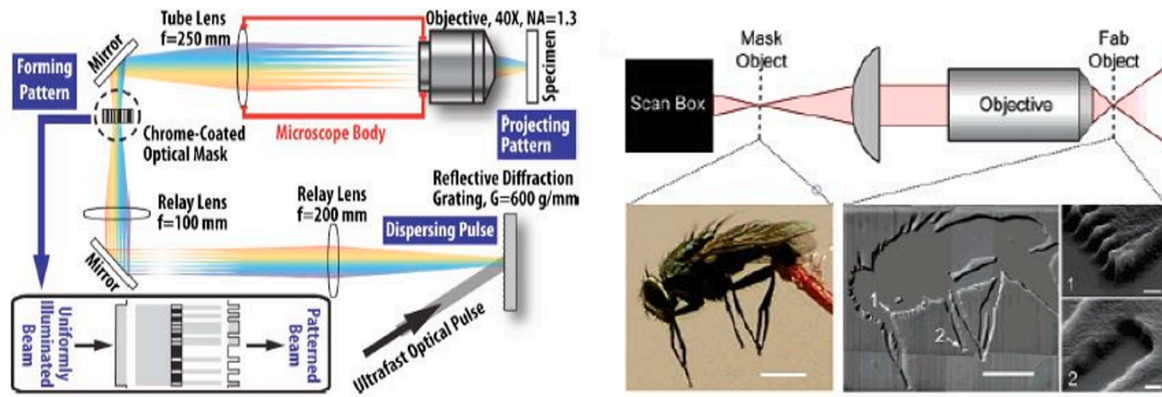


Fig. 12. (a) Schematic of TPL using optical masks for patterning [26]. (b) Schematic of TPL by placing an object as the mask in a plane conjugate to the front focal plane of the objective [89].

mirror device is a micro-opto-electro-mechanical system comprising several hundred thousand micromirrors arranged in a specific array, which correspond to the pixels of an image to be displayed. These micromirrors can be rotated about their own axis by certain angles to attain their optical state (on/off). Integration of both systems viz., MLAs and DMDs in TPL has produced a substantial decrease in the fabrication time. A multi-focal strategy has also been used by many groups to speed up the fabrication time [61,86]. In this approach, highly amplified laser beams are directed into an array of the lens, which is split into several low power beams brought to the voxel through a single microscopic objective. Hundreds of objects could be fabricated in the time ordinarily required to produce an individual structure. However, the fabrication time saved was significant only when creating replicas of a single structure. On the contrary, Nielson et al. [87] demonstrated the multi-focal strategy integrated with dynamic reflectance masks and DMDs to rapidly print non-repeating objects by utilizing multiple laser beams simultaneously to sample different regions on the DMD as shown in Fig. 11. It was also found that the duration for fabrication halved when two laser beams were used. Likewise, Wang et al. [88] presented a new random-access DMD scanner strategy by controlling the amplitude and phase of the laser via binary hologram and achieving fabrication speeds

of 5 mm/s per laser. Complex overhanging structures that are challenging and time-consuming were fabricated at a faster rate without compromising the resolution when compared to point scanning-based systems. This breakthrough is among the highest fabrication speeds achieved to date available in published literature. Similarly, Daekeun et al. [26] demonstrated the wide-field layer-by-layer fabrication of structures using optical masks incorporated with a high numerical aperture objective. Fig. 12 (a) presents the schematic of the system utilized by the group. One of the main characteristics of this technique is scalability, viz., the fabrication speed is not dependent on the size of features. However, such techniques are limited by the available peak input power and type of optical mask utilized. Regenerative amplifiers may be used to provide initial high input power to the system. Kaehr and Shah [89] demonstrated mask-directed multiphoton lithography by placing an object such as *Musca domestica* within the mask plane placed conjugate to the front focal plane of the objective. The object's negative was printed at the objective focal plane as shown in Fig. 12 (b). However, the positioning of the mask along the optical axis is the key to achieving the highest possible resolution. A small shift in the order of millimeters can degrade the resolution greatly. Dynamic digital masks incorporated with DMDs have proven to be a better alternative to

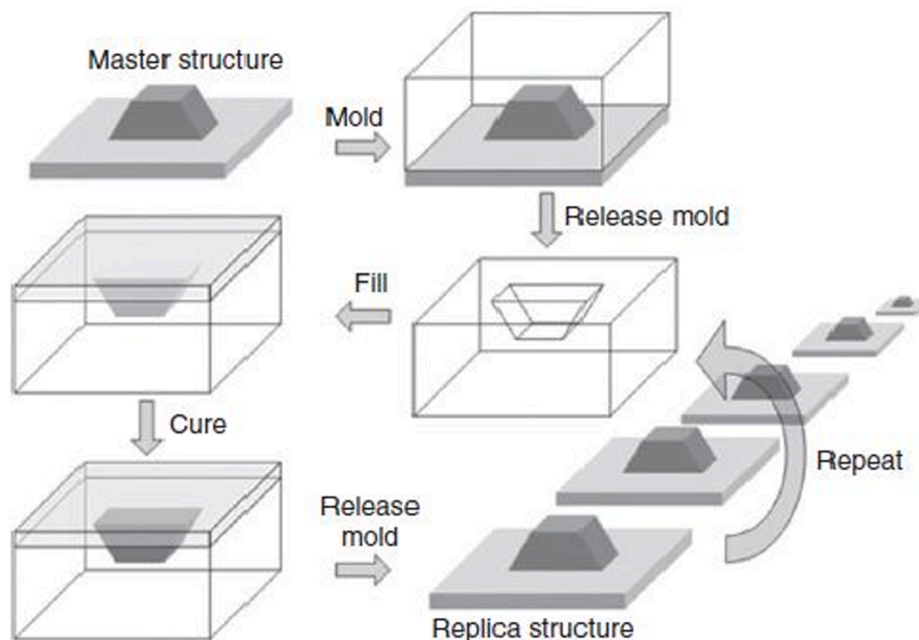


Fig. 13. Schematic of the replication of microstructures from a master template fabricated via TPL. [65].

physical masks if the structure is complex and requires multiple masks. Recently, Saha et al. [90] developed a femtosecond projection TPL (FP-TPL) method that ensures both spatial and temporal focusing to achieve parallel fabrication without compromising the resolution of the features. This was achieved by fabricating 3D structures using a layer-by-layer approach of patterned 2D layers with thickness ranging from $\sim 1 \mu\text{m}$ to $\sim 4 \mu\text{m}$. The patterning of 2D layers was performed using DMDs. Temporal focusing was ensured by progressively shortening the light pulse as it traveled through the photopolymer, i.e., the writing is spatially limited to the focal plane and polymerization is restricted only to that plane. Nanowire features with sub-diffraction feature sizes in both axial and lateral directions were printed by varying certain laser parameters. Furthermore, they also claim that this technique increases the throughput speed by approximately three orders of magnitude. The main advantages of this technique are the high throughput speed and wide-field fabrication. However, stacking up 2D layers to fabricate a 3D structure has its own limitations and disadvantages in terms of fabrication speed and axial resolution.

Parallel fabrication of features can be achieved by either using micro-lens arrays (MLAs) or spatial light modulators (SLMs). They can generate multiple laser foci from one single power unit combined with regenerative amplifiers. However, the bottleneck of using a stage scanning system to specify the fabrication coordinates results in the production of identical structures. Incorporating DMDs allows modulating multiple laser beams, thus resulting in the parallel fabrication of unique features. It is important for the incoming laser beam to be homogeneous for uniform replication. Varying power intensities after passing through the MLAs can cause a difference in the dimensions of the fabricated features. Similarly, SLMs can also generate multiple foci from a single beam source by providing control over the intensity and phase of the laser wavefront at different locations within the beam. Unlike MLA, in SLM, computer-generated hologram patterns are given as input, which are dynamic and can be changed rapidly. Most of the SLMs utilize either an array of electronically addressable liquid crystal pixels or an array of deformable micromirrors (DMMs). The main advantage of SLM is the capability to holographically translate multiple laser foci for the parallel fabrication of unique features [65]. This feature can play an important role in low-viscosity resins where parts can curl, or buckle if the supporting structures are not fabricated first. Microstructures can also be fabricated at a faster rate by replicating a master structure as depicted in Fig. 13. In this technique, a 3D microstructure is first fabricated via TPL, which is called the master structure and is further utilized to fabricate replicas by a faster process called micro-transfer molding. The main advantage of such soft lithography techniques is that the high resolution DLW technique is required only for the master structure which acts as the template for replication of hundreds of copies fabricated at rapid speeds. It also caters to the need for diversification of materials. However, this technique is limited in the structural design of the master template.

Another advancement to improve the speed of fabrication is the utilization of translational stages for fast scanning over large areas. For extreme precision in trajectory and position control with nanometer-range noise in straightness and flatness, air bearings are used, which can move at a speed of few centimeters per second. However, due to the weight of the stages, acceleration of the stages is slow and needs to cover a certain distance to attain uniform speed. Similarly, synchronization of the motion of a laser with high-speed pulse output is an essential factor to be taken into consideration for laser processing. It is very critical for the pulses to be accurate and depend on various parameters, viz., laser input power, motion speed, and trajectory.

6. Metamaterials

Materials with excellent mechanical properties, optical properties, multiple functionalities with the least weight possible are always in high demand. The design of materials with such characteristics is a continual

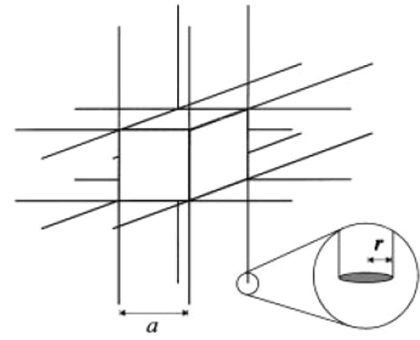


Fig. 14. Infinite wires arranged in a simple cubic lattice, joined at the corners of the structure [92].

goal for researchers and industries. Metamaterials is a rapidly emerging branch of science, which deals with the development of material properties out of the ordinary. Metamaterials are artificial materials or composites whose properties usually do not exist in nature, do not depend on the material composition, or do not depend on individual atoms, but largely depend on the fabricated structure topology. Metamaterials are derived from the Greek word “μετα” meaning beyond materials. TPL is an ideal technology for the fabrication of three-dimensional metamaterials as most of the elements do not require post-processing. Historically, the pursuit of metamaterials and phononic crystals was the primary motivation for the development of TPL technology.

Electromagnetic metamaterials are of great attraction to researchers, which usually involve cells with subwavelength geometries. Among the many types of electromagnetic metamaterials, plasmonic metamaterials stand out because of the unprecedented optical functionalities like a negative index of refraction, negative permeability, negative permittivity that can be obtained at will and cannot be realized in materials available in nature. These materials make good use of surface plasmons, which are collective oscillations of free electrons at metal-dielectric interfaces. Surface plasmon resonance (SPR) occurs when a light wave of a certain wavelength reaches the interface, and most of the irradiant energy is transferred to a surface plasmon of a shorter wavelength. The creation of plasmons on the surface of nanoparticles is called localized surface plasmon resonance (LSPR) and is guided by the shape, spacing and orientation of the nanoparticles. Manipulation of these parameters can result in metamaterials with unique mechanical and optical functionalities.

In 1968, Veselago [91] suggested the phenomenon of negative refractive index by materials whose permittivity (ϵ) and permeability (μ) were negative, which indicates the velocity of light within the material would also be negative. Although there are materials in nature with negative permittivity, there is none with both parameters being negative. Metamaterials were first experimentally proposed by Pendry et al. in 1996 [92]. Thin metallic wires with radius in the order of $\sim 1 \mu\text{m}$ were manufactured and assembled to form a simple cubic lattice structure illustrated in Fig. 14. The effective plasma frequency of the artificial material was depressed by up to 6 orders of magnitude, which subsequently changed the dielectric function of the material to a negative value. The effective permittivity is derived from the Drude-Lorentz model and is expressed as:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (10)$$

where $\epsilon(\omega)$ is the dielectric function, ω is the frequency of oscillation, ω_p is the plasma frequency of the material and γ is the damping term representing dissipation of plasmon's energy into the system ($\sim 0.1\omega_p$). Negative ϵ gives rise to a variety of electromagnetic structures decorating the surface of metals with a complexity controlled by the



Fig. 15. left-handed metamaterial (LHM) with square copper SRRs and copper wire strips on fiberglass circuit board material [93].

geometry of the surface [92].

Metamaterials have been studied for several unique properties and applications viz. negative index of refraction [93–96], invisibility cloaking [97–99], and superlensing [100]. TPL is a promising method for the fabrication of true 3D plasmonic metamaterials. Although TPL is limited in options for direct fabrication of 3D metallic structures, polymer-based resins can be embedded with metallic components by incorporating various deposition techniques. Split ring resonators (SRR) are a common application of electromagnetic metamaterials used to

produce artificial magnetism. Smith and coworkers [93], as represented in Fig. 15, realized 3D structures in the millimeter scale, operated in the microwave regime with a two-dimensional array of repeated unit cells of copper strips and SRRs on interlocking strips that exhibit a frequency band where the effective index of refraction is negative. However, to achieve magnetic resonance at optical frequencies, the SRR structure must be less than 100 nm in structure dimension with a gap less than 10 nm. Moreover, the scaling principle also starts to break down at higher frequencies as the metal significantly deviates from an ideal conductor [101].

However, Dolling et al. [102] overcame this problem by employing nanoscopic plate pairs or cut-wire pairs to produce negative permeability and negative permittivity directly, without employing SRRs as shown in Fig. 16 (a). In their design, the split in a normal SRR is opened, which consequently decreases the capacitance, C , and in turn increases the LC resonance frequency given by $\omega_{LC} = \frac{1}{\sqrt{LC}}$. Additionally, the bottom arm in the U-shaped structure is removed to produce cut-wire pair with length, l , thickness, t , width w , and the spacing between the wires, d . This furthermore decreases the net capacitance and increases the magnetic resonance frequency. Although it is straight-forward to achieve this design, the ratio of wavelength to the lattice constant, λ/a , must be very high for true metamaterials. In this case, the ratio is typically low (~ 2). However, when $l = w$, the cut-wire pairs behave like nanoscopic plate pairs with more pronounced optical resonance relative to cut-wire pairs. In contrast to the theoretical studies, a negative refractive index, however, was not obtained although negative permittivity and permeability were achieved.

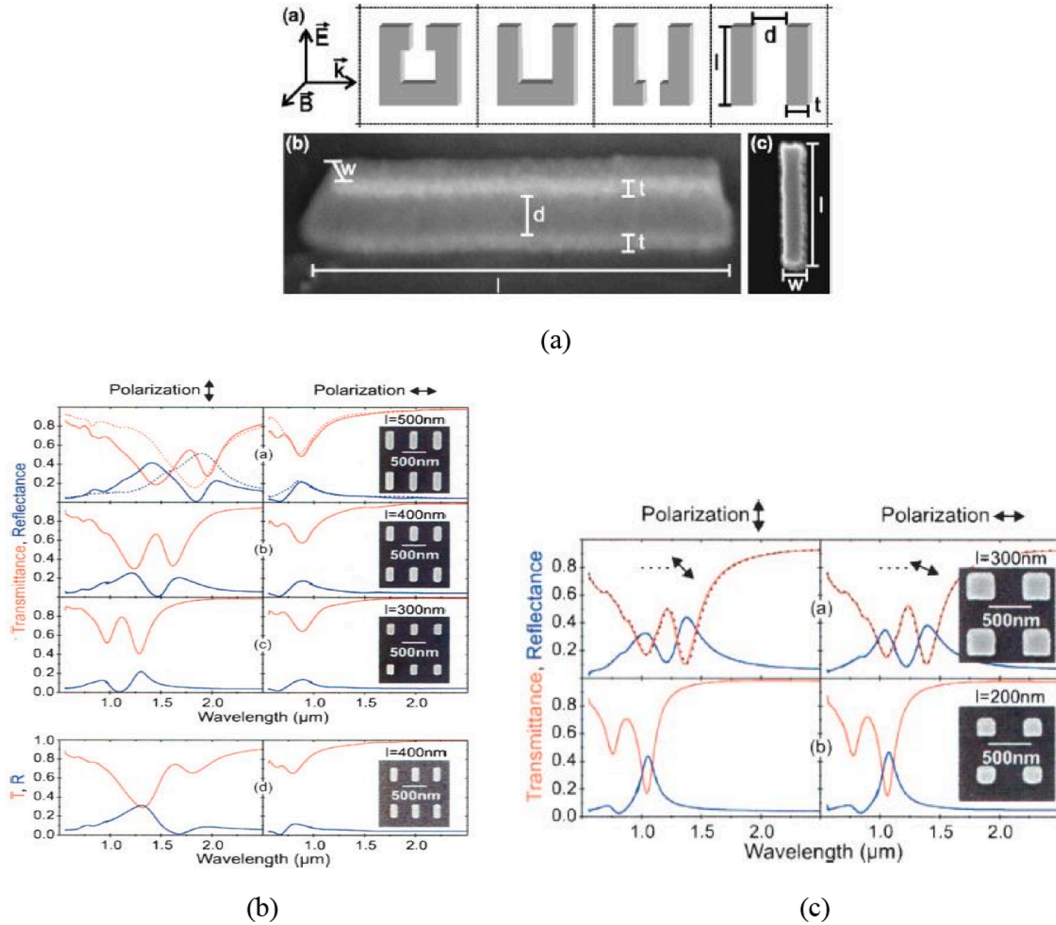


Fig. 16. (a) Schematic of adiabatic transition from SRRs to cut-wire pairs. (bottom left) one cut wire placed on top of another with a certain dielectric spacer layer in between. (b) Measure transmittance (red) and reflectance (blue) for cut-wire pairs. Insets correspond to electron micrographs. (c) measure transmittance (red) and reflectance (blue) for arrays of plate pairs. From [102].

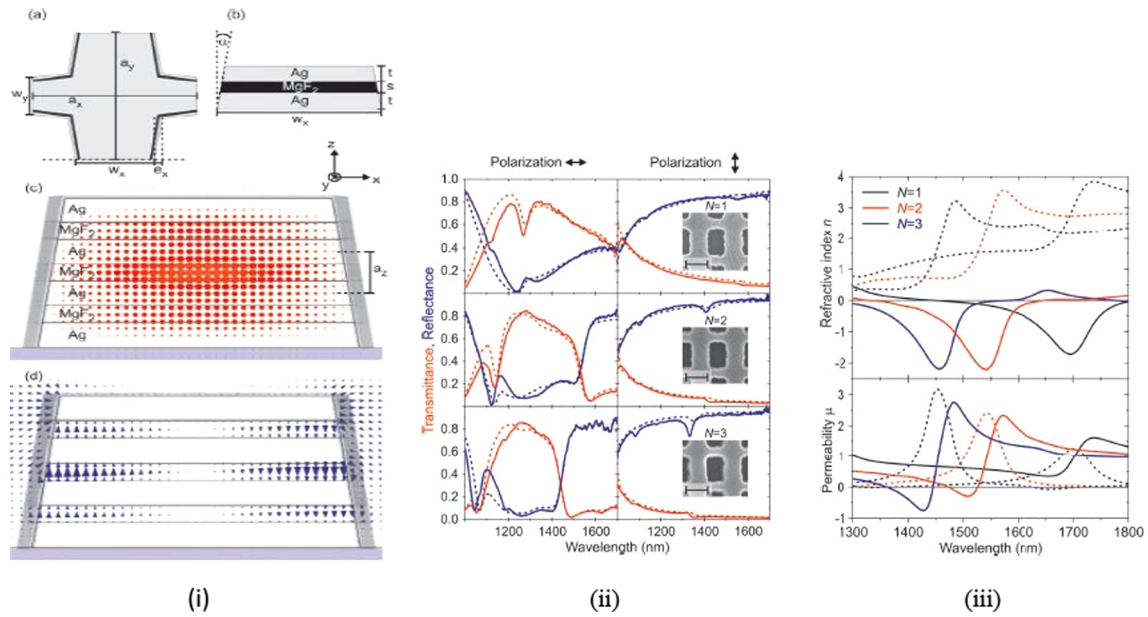


Fig. 17. (i)(a) Top view of one unit cell of the functional metamaterial. (b) Side view. (c) magnetic field (linear scale) for $N = 3$ and a wavelength of 1430 nm. (d) Electric field (linear scale) for same plane and wavelength. (ii) Measured (solid) and calculated (dashed) normal incidence transmittance (red) and reflectance (blue) for $N = 1, 2, 3$ functional layers respectively. Insets correspond to electron micrographs with a 400 nm scale. (iii) Effective refractive index (top) and permeability (bottom). Real parts, solid, imaginary parts, dashed. From [103].

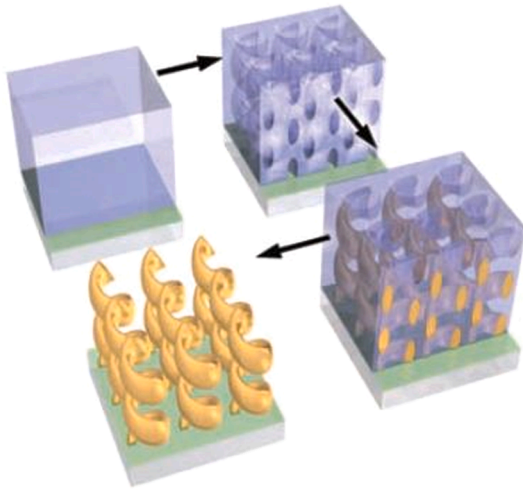


Fig. 18. Flow of fabrication of gold helix plasmonic metamaterials. (top left) A positive-tone photoresist is deposited onto a glass substrate with a ~ 25 nm thin layer of ITO (green). (top right) An array of helices fabricated in the photoresist. (Bottom right) After electrochemical deposition of gold onto the template. (bottom left) self-standing helical structures obtained after removing the photoresist via plasma etching. From [104].

In 2007, Dolling and colleagues [103] claimed to be the first ones to fabricate one, two and three-functional layer metamaterials. The process started with a single functional layer producing negative magnetic permeability above the magnetic resonance frequency and negative electric permittivity below the effective plasma frequency successively generating a negative index of refraction. To expand the structure to three dimensions, multiple layers of metal-dielectric-metal were stacked as represented in Fig. 17 (i). They used 31 nm thick silver and 21 nm thick MgF_2 as the metal and dielectric layers respectively resulting in a high ratio of wavelength to lattice constant (~ 27), although they could experimentally fabricate only up to 3 functional layers (7 real layers) through electron beam lithography (EBL). Fabrication of thicker

structures is much more difficult through EBL because of the dependence of total thickness on the thickness of the patterned electron beam resist. The total thickness is limited to, at maximum, 80% of the thickness of the resist, which is close to ~ 100 nm for EBL. The issue of a stepped wall also arises if the thickness is high.

Though stacking up 2D layers via EBL or focused ion beam (FIB) forms 3D metamaterials in principle, inherently they are 2.5D, i.e., 2D structures with multiple functional layers. Furthermore, the process is slow, expensive and requires a lot of skill to achieve proper alignment. In order to obtain true 3D metamaterial structures, TPL can be employed. It is best suited, and the process can be expedited by integrating optics like MLAs, DMDs as discussed earlier.

Gansel et al. [104] fabricated a true 3D helical free-standing metamaterial structure via TPL as depicted in Fig. 18. The process started with the usual split-ring resonators and adiabatically pulling one end of this planar SRR out of the fabricating plane, thereby resulting in a circular helix of gold structures with electromagnetic modes close to that of an SRR. They used a positive-tone photoresist to fabricate the template and infilled it with gold by electrochemical deposition because of its excellent optical properties at mid-infrared wavelengths. Subsequently, they removed the polymer through plasma etching. Initially, for the purpose of electrochemical deposition, the glass substrate on which fabrication was performed was deposited with a thin film (~ 25 nm) of indium tin oxide (ITO) acting as the cathode. However, the electroplating process is not applicable to many complex designs like structures with interlockings, suspended features and chirality. The parameters like electroplating time, the direction of electroplating, bath temperature, current density, solution concentration define the thickness of the coating. Manipulation of these parameters simultaneously to obtain the desired coating is cumbersome and time-consuming. Similarly, in 2017, Frenzel et al. [105] fabricated the elastic counterpart of optical activity in 3D chiral structures. i.e., 3D chiral mechanical metamaterials with a twisting degree of freedom extending beyond the Cauchy elasticity.

Mu and coworkers [106] fabricated metallic pyramids plasmonic metamaterial via TPL followed by electron beam evaporation. Initially, keeping a copper grid as the substrate, a negative photoresist was used to fabricate the pyramid template via TPL. This was followed by electron beam evaporation of silver onto the hollow pyramid surfaces. These

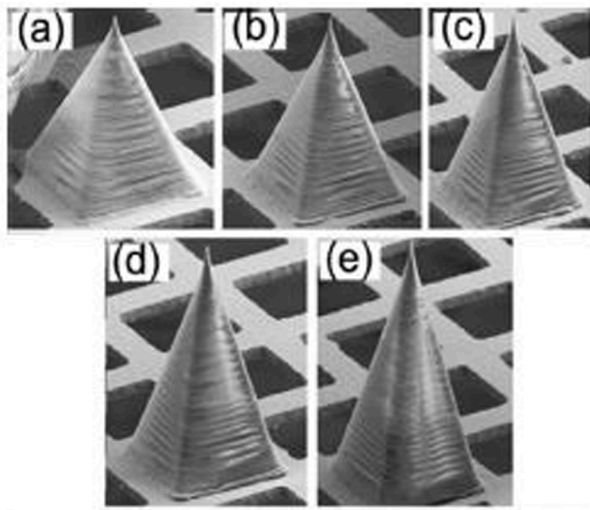


Fig. 19. SEM images of hollow silver-coated metallic pyramid structures with 50.60.70.80.90 μm in height, respectively. From [106].

metallic pyramids can be used as surface-enhanced Raman spectroscopy (SERS) substrates for their electromagnetic properties. However, the stepped wall effect became prominent as the height of the structure increases as shown in Fig. 19.

Electroless plating is an alternative metal deposition technique to overcome the limitations in electroplating. It is a wet-chemical metallization technique on a catalytic surface based on an autocatalytic redox reaction without any external current dependency. A reducing agent added to the solution reduces the metal particles from their ionic state before deposition. The quality of deposition is determined by the adhesion between the metal particles and the surface. Radke and co-workers [107] used this technique along with TPL to fabricate three-dimensional bichiral plasmonic crystals as shown in Fig. 20. Initially, they fabricated a 3D bichiral crystal template via TPL in a negative-tone photoresist. Eventually, this template was coated with silver via electroless silver plating. However, during the process of electroless plating, the glass substrate was coated with silver as well. In order to overcome this effect, the crystal had to be detached from the coated substrate and placed onto a neat glass substrate. However, detaching the crystal from the bottom created holes in the silver film at the point of contact. Therefore, they set up vertical posts at the corners as shown in Fig. 20 (b). These posts served as spacers between the crystal and the substrate making it easier to remove after the plating process. Although, when compared to electroplating, the process is faster and accurate, it is

cumbersome and requires expertise to carefully remove the structure from the substrate and place it onto a cleaner glass substrate. Similarly, Chen et al. [108] fabricated 3D silver-coated polymeric microstructures. In their method, the 3D microstructure template after TPA was functionalized with alkylamines by treating with $\text{NH}_2(\text{CH}_2)_3\text{NHLi}$. This strong nucleophile cleaves exposed acrylate esters, creating surface-bound amine termination. Gold particles were then bound to the amines by immersing the template structure in aqueous AuCl_4^- and reducing with NaBH_4 . Silver metal was then deposited onto the structure via electroless plating. The deposition is effective only on the surfaces treated with both aminolysis and $\text{AuCl}_4^-/\text{NaBH}_4$ reagents. In this way the extra step of transferring the microstructure to a clean substrate was eliminated. However, the main disadvantage of such techniques is that the density of the metal-binding sites onto the template cannot be controlled. The quality of metallization depends on the adhesion between the metal and the surface, which cannot be manipulated easily. Therefore, site-selective electroless plating is a viable alternative.

Kawata et al. [109] demonstrated the fabrication of 3D metal/polymer microstructures via TPL and site-selective electroless silver plating. In their experiment, activated and non-activated resins were utilized for the fabrication of complex metal/polymer 3D microstructures. Initially, a laser beam was focused onto the non-activated monomer and after the exposure, the uncured resin was washed away with acetone. Eventually, a small amount of activated resin was dripped onto the polymerized structure and the same procedure was followed to form pairs of polymer layers on a glass substrate. Later, the fabricated polymer samples were immersed in an aqueous solution of AgNO_3 for a period of close to ~ 6 hrs. After the treatment, the activated resin parts

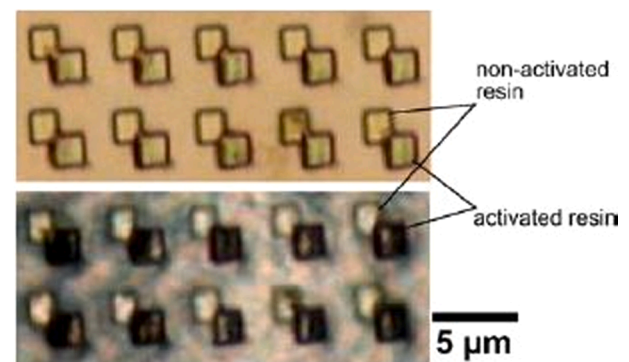


Fig. 21. Microscope images of pairs of polymer sheets made via TPL with activated and non-activated resin. (Top) after soaking in AgNO_3 aqueous solution for 6 h. (bottom) After electroless plating. From [109].

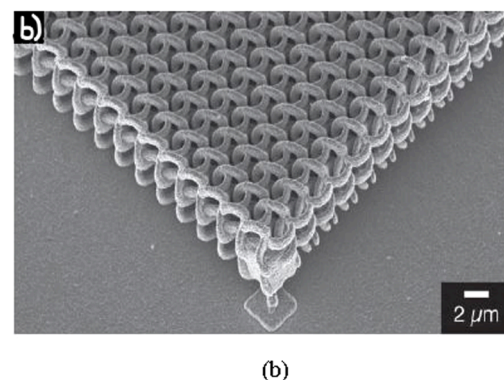
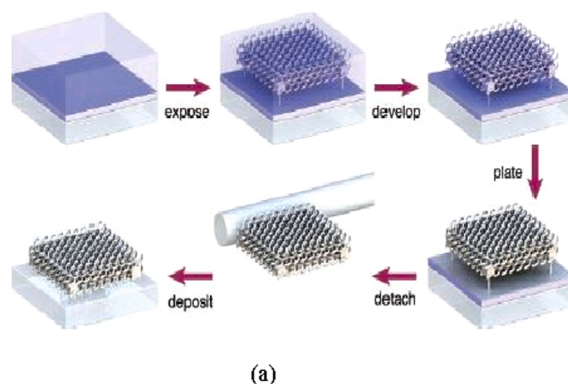


Fig. 20. (a) Flow of fabrication. A glass cover slip serves as the substrate on which a negative-tone photoresist is deposited via spin-coating. TPL is used to fabricate the template structure. Post-baking and developing generate a free-standing template of the 3D bichiral crystal structure. All surfaces of the template including the substrate are coated with a conformal silver via electroless plating. To facilitate transmission spectroscopy, the crystal is detached from the template and deposited onto a clean glass substrate with a thin glass capillary. (b) oblique view of the bichiral structure after electroless plating. From [107].

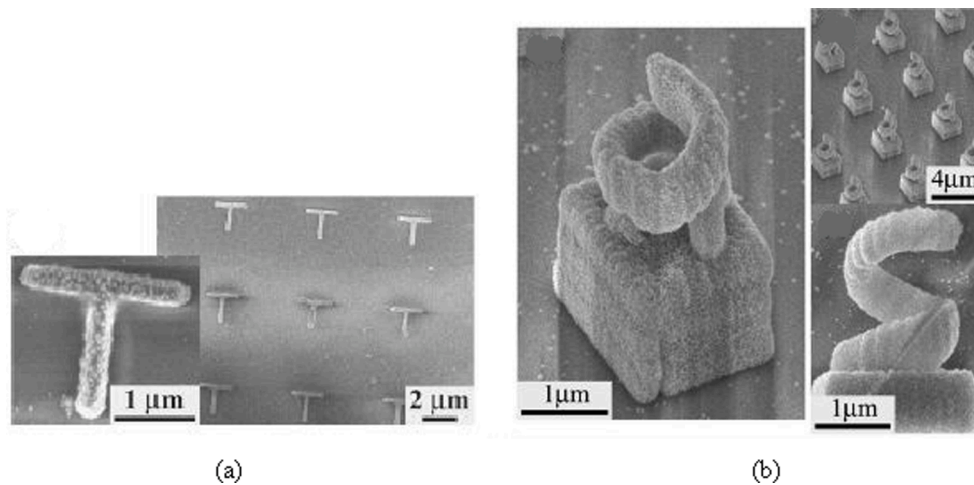


Fig. 22. (a) SEM images of 2D polymer structures selectively coated with small silver grains. (b) SEM images of a silver-coated polymer structure consisting of a cube supporting a helical structure. From [112].

appeared slightly darker due to the deposition of Ag nanoparticles onto the surface. Finally, when silver was coated onto the structures via electroless plating, the activated resin parts appeared opaque while the other parts appeared transparent in the transmission image as seen in Fig. 21, thus confirming the deposition of silver only in the desired sites. The main disadvantages of this technique are: there are limited metal-binding materials that can be utilized and the required resolution and structural integrity for optical metamaterials are not met in most cases. However, in 2012, Vasilantonakis and colleagues [110,111] demonstrated the possibility of fabrication of optical nanophotonic devices via TPL and selective electroless plating. 3D metallic woodpile structures with features below 100 nm were fabricated using an organic–inorganic, zirconium-silicon hybrid material doped with a metal-binding monomer followed by metallization through electroless plating. The metallized structures exhibited ohmic conductivity, comparable to pure silver.

Similarly, Formanek and coworkers [112] demonstrated the 3D

fabrication of metallic micro/nano structures based on TPL combined with electroless plating. MLAs were employed to produce numerous structures of the same pattern spread out over a large area. They also claimed their experiment to be one of the firsts to demonstrate the fabrication of true 3D metallic complex structures obtained from TPL. In their fabrication process, TPL was conducted inside a chemically modified resin through MLAs producing multiple structures on a previously deactivated glass substrate. Initially, to obtain a deactivated substrate, glass slides were cleaned, dried and soaked in a 5% solution of dimethyldichlorosilane in toluene for 1 min and later washed with methanol producing a layer of hydrophobic coating. Subsequently, after the microfabrication process, the surface of the structures was pre-treated with SnCl_2 to improve metal adhesion with the polymerized resin. Finally, silver was deposited via electroless plating producing thickness-controlled, uniformly coated self-standing metallic 3D structures as shown in Fig. 22 (b). This metallization technique can produce

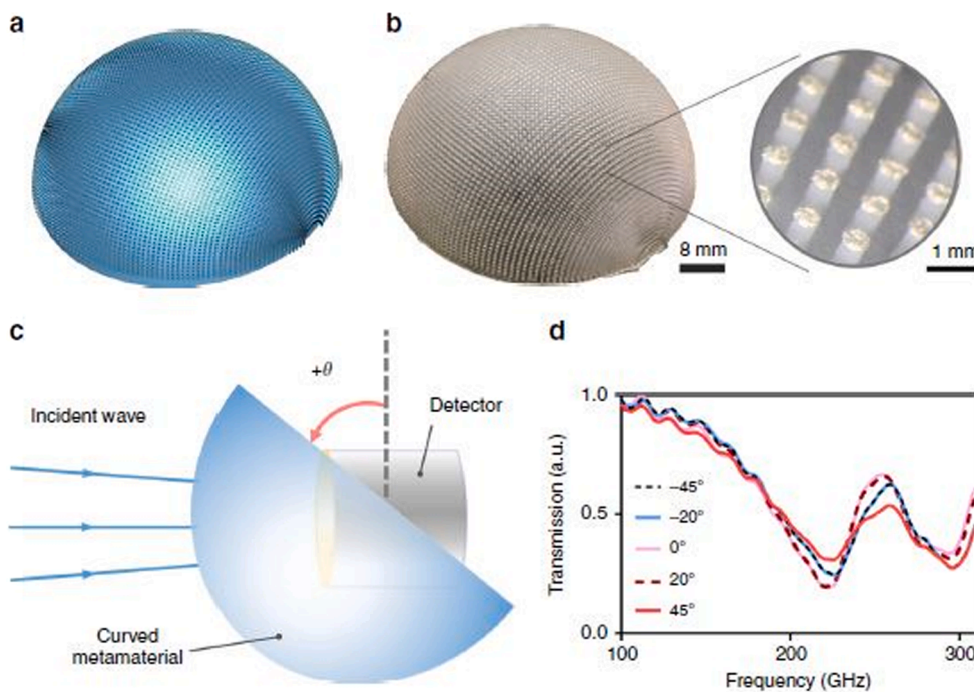


Fig. 23. a) CAD model of the moth-eye MEGO absorber. b) fabricated and silver-coated structure. c) schematic of the device in different propagation angles as a function of θ . d) transmission spectrum of the absorber as a function of θ . From [116].

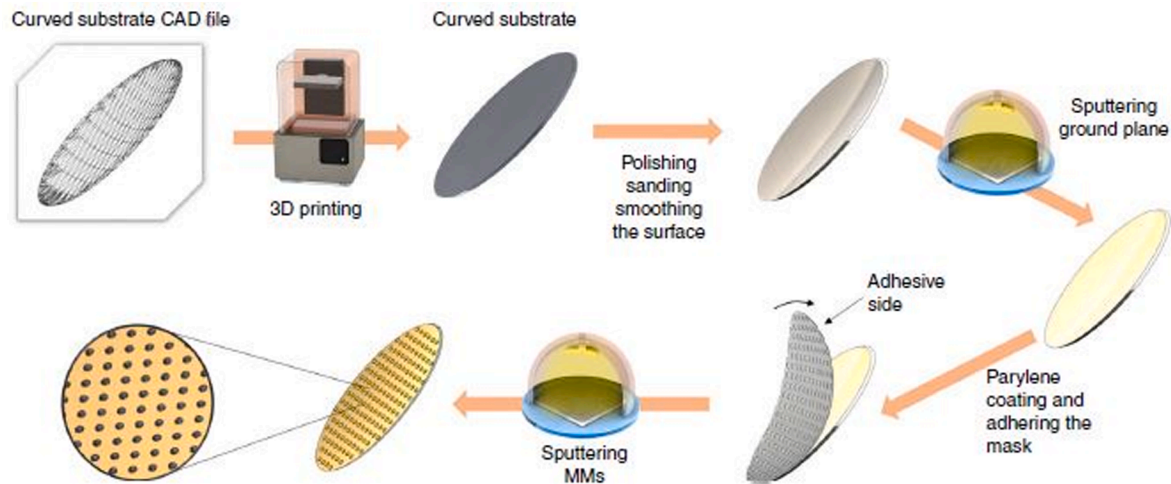


Fig. 24. Fabrication flow of MEGO parabolic reflector. From [116].

numerous highly conducting structures by making the substrate hydrophobic or can also produce hundreds of isolated insulators on a metallic coated substrate.

Rill et al. [113] demonstrated the fabrication of photonic metamaterials via TPL combined with silver chemical vapor deposition. Their experiment started with a glass substrate covered with a 2 μm thick, fully polymerized SU8 film. Subsequently, another film was spin-coated on the substrate and the template was fabricated via TPL. The template was later coated with SiO_2 via ALD with SiCl_4 as the precursor, which was performed to provide mechanical stability, thermal resistance, and chemical protection to the template during CVD of silver at 160 $^\circ\text{C}$. The activation of the coated surface was performed by exposing it to O_2 plasma for 15 min. Each static cycle during CVD deposited approximately ~ 5 nm of silver. The structures fabricated by them are results of 10 CVD static cycles, i.e., deposition thickness close to ~ 50 nm. The crucial aspects that can be inferred from their method are that the coating is uniform even in 3D, silver exhibits good dc conductivity, magnetic permeability and exhibits magnetic resonance at near-infrared frequencies with $\text{Re}(\mu)$ less than 0 and the process is quick.

Line of sight deposition techniques such as thermal evaporation and sputter coating can also be integrated with TPL to realize true three-dimensional metamaterial structures rapidly. Sputtering techniques are mostly used for the deposition of metal and oxide films by controlling the crystalline structure and the surface roughness. For effective sputtering, the bombarding ions and the atoms being bombarded must be of the same atomic weight to maximize the momentum transfer. Several groups [114,115] have utilized this technique along with TPL to deposit metal nanoparticles in order to obtain desired magnetic properties. Sadeqi and colleagues [116] took it further by fabricating several kinds of metamaterials via TPL. Metallization was performed by two techniques namely, stamping (manually dipping the template into a metal paste) and sputtering. They compared the two fabricated structures and proved experimentally that the sputtering technique produced relatively uniform thickness coating. However, in one of their novel metamaterials embedded geometrical optics (MEGO) designs called an omni-directional hemispherical moth-eye absorber which resembles a moth-eye as shown in Fig. 23 (a), the coating was performed via stamping. This was because sputtering and wet etching are not suitable for curved substrates. They also claim that this metamaterial is the first ever realization of an angle-insensitive narrow-band metamaterial absorber fabricated on a curved substrate. They state that such elements can be incorporated in future cloaking devices for enhanced optical properties. Integration of an optical parabolic reflector with a frequency selective metamaterial-based transmissive filter was also performed to realize a unique parabolic MEGO reflector device as shown in Fig. 24. It

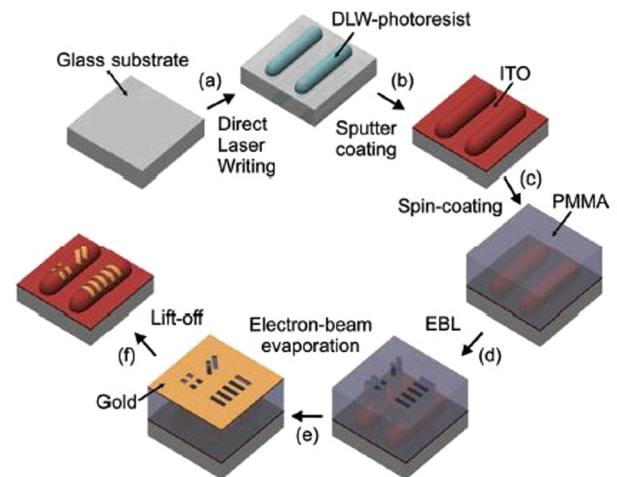


Fig. 25. Schematic of the process of hybrid 3D nanofabrication via TPL and EBL. From [118].

was designed in such a way that the MEGO reflector reflects the beam at a single focal point for selective frequencies where a detector can be placed.

Fabrication of complex structures incorporating hybrid polymer templates with multiple photoresists deposited on top of another and polymerized sequentially has also been demonstrated [117]. Integration of various techniques to write on the different resists can be performed to obtain enhanced material properties with superior resolution. Generally, two different photoresists are deposited on the same substrate over one another and the top layer is used as the sacrificial stencil mask which is later removed via appropriate post-treatment. This technology can be utilized to a good advantage for the deposition of metal nanoparticles uniformly onto the polymer templates for various photonic and metamaterial applications. However, while TPL allows for the fabrication of arbitrary complex structures, the feature sizes obtained are too large for optical frequency applications. Although STED and PInSR are considered to produce enhanced structures with superior resolution, the metallization of the template selectively becomes an issue.

Staudte and team [118] overcame this problem by exploiting the technology of multiple photoresists and integrating several technologies like TPL and EBL in combination with metal-evaporation and standard lift-off procedure to produce high resolution 3D metallic structures coated selectively and evenly as shown in Fig. 25. In their technique,

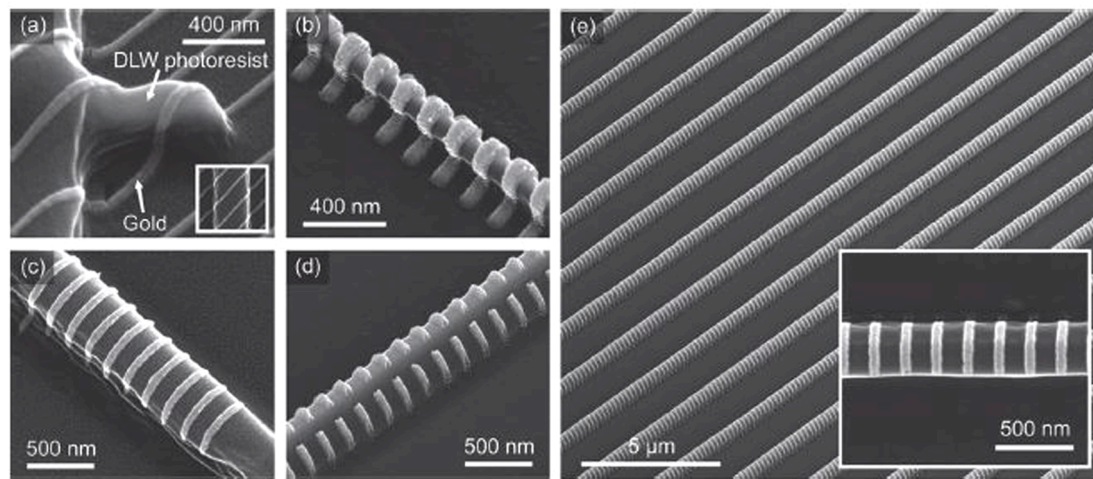


Fig. 26. SEM images of several structures realized from hybrid nanofabrication technology. (a) selective metallization. (b) Short gold nanowires aligned with respect to the TPL photoresist lines to form Ω -shaped structures. (c)-(d) 3D nanoantennae inspired by various designs. (e) A 2D array of upright standing SRRs. From [118].

initially, the glass substrate was spin-coated with IP-L negative tone photoresist and TPL was performed and developed to produce permanent 3D polymeric structures. Eventually, the developed photoresist was sputter-coated with ITO to prevent charge accumulation at the surface during EBL. Later, a sufficiently thick layer of PMMA was spun onto the same substrate over the polymerized structure. EBL was then employed to write high resolution pattern on the PMMA. After the development of PMMA, a 50 nm thick gold film was deposited onto the sample pattern by electron beam evaporation. Finally, a standard lift-off procedure was used to remove the PMMA and these gold patterns were embedded onto the two-photon polymerized structures uniformly at desired locations as shown in Fig. 26. However, the standard lift-off procedure does have some major drawbacks such as retention and redeposition.

Although TPL has been considered a promising technology for the development of photonic crystal (PhC) design largely due to its 3D processing capability, many researchers have failed to fabricate structures demonstrating the photonic bandgap (PBG) effect. Considering a log pile structure, it is certain that the rod diameter is not uniform due to the acceleration and deceleration effects of the piezo stage moving with a uniform scan speed. This directly hinders the flow of non-polymerized resin resulting in incomplete resin-air lattices. Similarly, the height and width of the structure are defined by the laser exposure dose and numerical aperture of the objective. Since they cannot be manipulated independently, the lattice parameters including in-plane filling ratio and layer interval are difficult to optimize separately. These factors have been identified as the major reasons for no PBG effect in PhC fabricated via TPL. Sun et al. [35] proposed and demonstrated a technique to overcome this problem. They quantified the entire 3D space of fabrication into uniformly spaced voxels instead of defining a rod by single-line scanning. During fabrication, the laser raster scans the entire 3D space but stops only at certain prescribed points for a given duration and irradiates the resin to define the structure. Additionally, structure deformation in the transition layer was also taken care of by using a pre-compensation strategy considering that the shrinkage rate from liquid to solid is material dependent and experimentally measurable.

In another approach by Yinan and coworkers [119], a self-developed sol-gel material prepared using a sol-gel organic-inorganic hybrid technology called the SZ2080 was utilized for the fabrication of photonic crystals via TPL. This material possessed a unique property of very negligible shrinkage eventuating before polymerization. This material was employed to fabricate 3D woodpile structures with periodicity in every four layers. Although the ratio of the refractive indices of SZ2080 and air was around 1.5 (less than 2), band gaps were observed along the stacking direction.

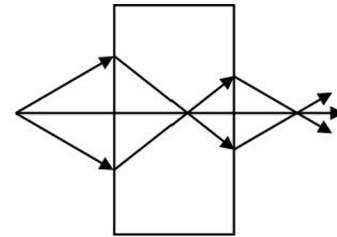


Fig. 27. A NIR metamaterial initially bending light to a negative angle with the normal and eventually converging to a point on the back of the lens forming an image. From [120].

Besides magnetic resonance imaging, a perfect lens with resolution beyond the governing diffraction limit is one of the most sought out subjects. Resolving two points with spacing less than $\frac{\lambda}{2n}$, where n is the index of refraction, is impossible with conventional optical systems. This is because the features of the object are carried by evanescent waves which exponentially decay before reaching the image plane. In order to overcome this, Pendry [120] proposed a negative index of refraction (NIR) metamaterial which uses the properties of both evanescent and propagating waves forming a perfect lens for imaging beyond the diffraction limit. Fig. 27 depicts the working of a NIR metamaterial for imaging.

Transformational optics is a rapidly growing branch of optics that deals with precise control of light path by spatially tailoring the material property governed by Fermat's principle, the law of refraction, and Snell's law. Invisibility cloaking and superlensing are some of the applications of transformational optics. As depicted in Fig. 28 (a), a superlens consists of a thin silver slab separated from the object ("NANO") by a spacer layer and coated with an imaging material on the opposite side carefully designed in a such a way that the surface plasmons match the evanescent waves from the object. The key aspect for perfect lensing is the enhancement of the evanescent waves by the surface plasmons. Although experimentally many groups failed to achieve resonance with accurate thickness, Fang et al. [100], as shown in Fig. 28 (a), experimentally demonstrated this technique using a 35 nm silver film evaporated over a PMMA spacer layer and a subsequent 120 nm thick coating of a negative photoresist and the object being placed at a distance of 40 nm from the film. Atomic force microscopy (AFM) was used to develop the image obtained from the superlens, which resulted in a 60 nm half-pitch resolution. The captured image replicated the fine features of the object mask in all directions consistently as seen in Fig. 28

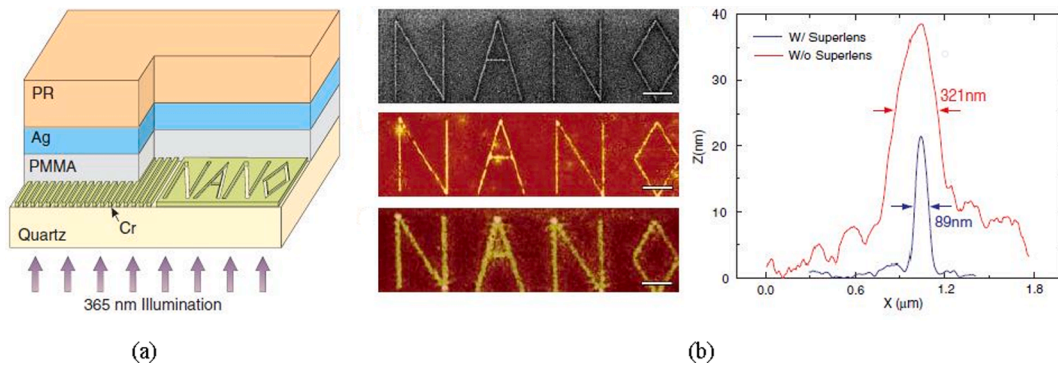


Fig. 28. (a) The object to be captured is inscribed onto a 50 nm thick chrome (Cr); at left is an array of 60 nm wide slots of 120 nm pitch. At right is the inscription of the word “NANO”. All separated from the 35 nm silver film by a 40 nm PMMA spacer layer. The image is recorded by the photoresist on the opposite side. (b) FIB image of “NANO” (top); AFM of the captured image (center) on the photoresist; AFM of the captured image (bottom) without the 35 nm silver film. The average line width obtained with the silver film was found to be ~ 89 nm and without the film was found to be ~ 321 nm. From [100].

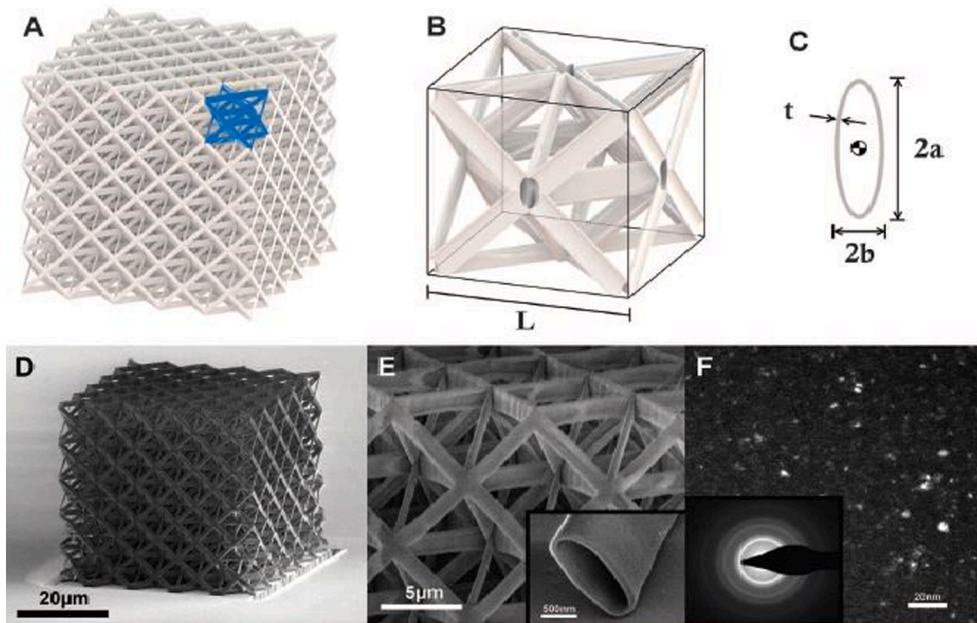


Fig. 29. (A) CAD image of the octet truss design. (B) A single unit cell. (C) Elliptical cross-section of the hollow octet truss tube. (D) SEM image of the alumina octet-truss nanolattice. (E) Zoomed-in image. Inset showing the hollow tube. (F) TEM dark-field image with diffraction grating of the alumina nanolattice tube wall. From [123].

(b).

Mechanical metamaterials are also of great interest to researchers for their myriad of applications in mechanics. Among the various types of mechanical metamaterials, lightweight lattice structures are found to be fascinating. Most of the rigid materials with high strength-to-weight and stiffness-to-weight ratios such as diamond, metallic glass, or ceramics possess excellent strength and are light. However, their sub-par elastic nature and very low toughness hinder their suitability to many applications in lightweight mechanics. Composites are a good alternative, but again the increase in weight makes them less viable to lightweight applications. Many naturally occurring materials such as sea sponge *euplectella aspergillum* [121] and diatom shells [122], which are coincidentally stiff, tough, and light, are believed to arise mainly from the design of the structural components. Meza et al. [123] fabricated a strong, stiff, energy absorbing, hollow-tube nanolattice with an octet truss geometry that exclusively consists of brittle ceramic and alumina as shown in Fig. 29 (D-E). This structure exhibited almost complete recoverability after compressions in excess of 50% strain. It was also found that Young's modulus varied with the relative density as $E \rho^{1.61}$,

and the ultimate strength varied with a density as $\sigma_u \rho^{1.76}$ which differed from the analytical values because of the hollow tubes and nodes. The fabrication was performed starting with the two-photon polymerization of the 3D scaffold. Subsequently, thin layers of alumina were then deposited onto the scaffold via the atomic layer deposition (ALD) technique. The outermost walls of the structure after coating were removed via focused ion beam milling and the polymer scaffold was removed via O_2 plasma etching resulting in a 3D free standing nanolattice. Because ALD is a layer-by-layer approach, the thickness of the resulting layers of structures is entirely controlled by the number of deposition cycles.

In 2016, Bauer and group [124] took it further by fabricating ultra-strong, lightweight, nano-architected glassy carbon lattices via TPL and pyrolysis of the polymeric structures which could sustain compression stresses of up to ~ 310 MPa at a density of 0.35 g cm^{-3} . The polymeric nanolattices and nano-honeycomb structures were constructed by direct laser writing and subsequent pyrolysis in vacuum at a temperature of 900°C . During pyrolysis, these structures shrank isotropically by 80% in volume. Undistorted structures were obtained by

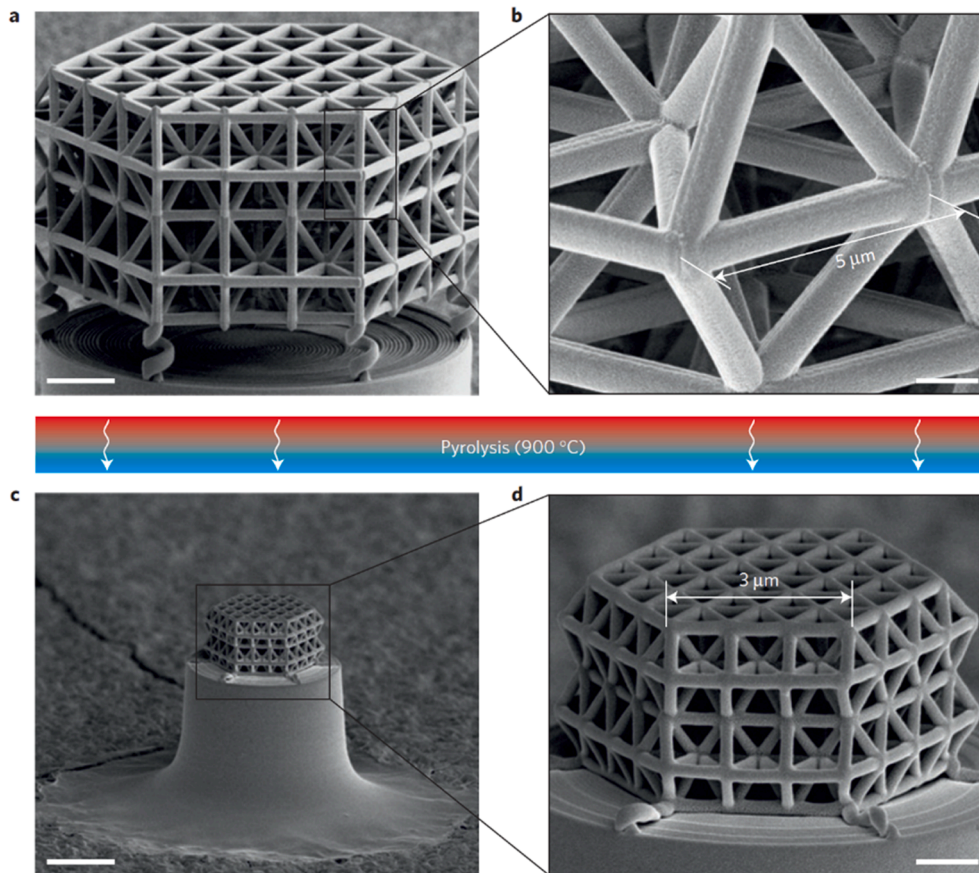


Fig. 30. (a) Polymeric 3D structure before pyrolysis. (b) Magnified image of a single unit cell. (c) shrunk nanolattice on a pedestal for easy removal from the substrate. (d) magnified image of the shrunk nanolattice. From [124].

placing the structures on pedestals and coiled springs for easy removal from the substrate as shown in Fig. 30. Interestingly, these significantly reduced feature sizes displayed unprecedented strength corresponding to the theoretical strength of bulk glassy carbon. Furthermore, these nanolattices represent the smallest lattice structures produced so far in published literature. It is evident that such structures possess great potential for mechanical and optical metamaterial applications.

In order to characterize mechanical metamaterials appropriately, the height of the overall structure must be high. TPL allows fabrication of structures typically with height in the range of tens of micrometers only. However, Buckmann et al. [125] proposed a novel “Dip-in” 3D DLW technique as shown in Fig. 31 (i). This method makes use of the photoresist itself as the immersion oil between the objective and the substrate extending the fabrication to millimeters in height with sub-micrometer feature sizes. They fabricated true 3D crystalline metamaterials in the micrometer range exhibiting adjustable Poisson’s ratios including negative values, i.e., compressing the material in the axial direction leads to a contraction in at least one of the lateral directions in uniaxial structures as well as huge mechanical nonlinearities starting from zero Poisson’s ratio. The structural design of their metamaterial was inspired by the bow-tie functional element represented in Fig. 31 (ii) (a). Fabrication of the 3D structures was performed by grouping these functional elements in different orientations as shown in Fig. 32. These structures were later subjected to compression loading along the z-direction to determine the Poisson’s ratio.

Similarly, in 2012, the same group [126] demonstrated the fabrication of pentamode three-dimensional mechanical metamaterials applying their novel “dip-in” 3D DLW with double cone lengths in the ten-micrometer range and with figures of merit (FOM) exceeding 10^3 .

Pentamodes, also sometimes known as metafluids, were first pro-

posed by Milton and Cherkav in 1995 [127]. They are unique because of their property that avoids coupling of compression and shear waves by increasing the bulk modulus, B , to an extremely large value ($\rightarrow \infty$) relative to the shear modulus, G . However, for the stability they replaced the fine point-like tips suggested by Milton and Cherkav with thicker overlap values ($d \sim 0.55 \mu\text{m}$) leading to the figure of merit values in the range of $\sim 10^3$. Figs. 33 and 34 represent the design and TPL fabrication of the pentamode metamaterial, respectively. Furthermore, they believe that a reduction of the critical dimension to $0.1 \mu\text{m}$ can increase the FOM to 10^4 .

Cloaking has been demonstrated in electromagnetism at various frequencies by many groups [91–93,128,129]. Although the implementation of cloaking in 3D structures is a cumbersome task, TPL has been a promising technology to achieve 3D cloaking. Fischer and his team [77] were among the first groups to demonstrate three-dimensional invisibility cloaking in the microwave frequencies ($\sim 1.5 \mu\text{m}$). They employed STED-inspired-TPL to fabricate the 3D woodpile-like polymeric structures. In 2011, the same group [130] demonstrated 3D invisibility cloaking in the optical frequencies by miniaturizing all the features in their previous experiment by a factor of 2. The lattice spacing was scaled down to 350 nm from 800 nm and according to Maxwell relations, the operating wavelength scaled down from $1.5 \mu\text{m}$ to $0.7 \mu\text{m}$ (visible red). The modifications in this experiment from the previous experiment included the employment of a different photo-initiator and a suitable phase mask for enhanced lateral and axial resolutions. In order to investigate the action of cloaking, they fabricated two structures: 1) reference structure and 2) cloaking structure with a $\cos^2$ -function like indentation on the top surface of both as shown in Fig. 35 (a). Both these structures were sputter-coated with 100 nm of gold after TPL for enhanced visibility prior to the indentation. Cloaking

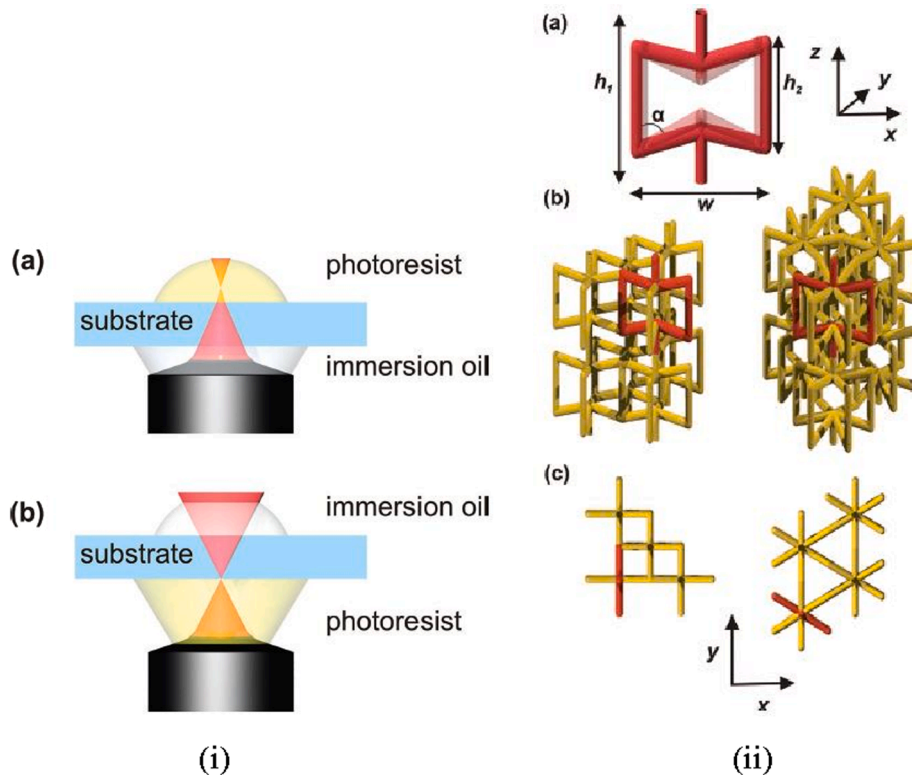


Fig. 31. (i) a) Schematic of regular DLW. b) Schematic of novel “Dip-in” 3D DLW. (ii) a) Bow-tie functional element. b) Trilinear crystal structure with four-fold rotational axis (left) and six-fold rotational axis (right) respectively. (c) top view of the respective images in (ii)b). From [125].

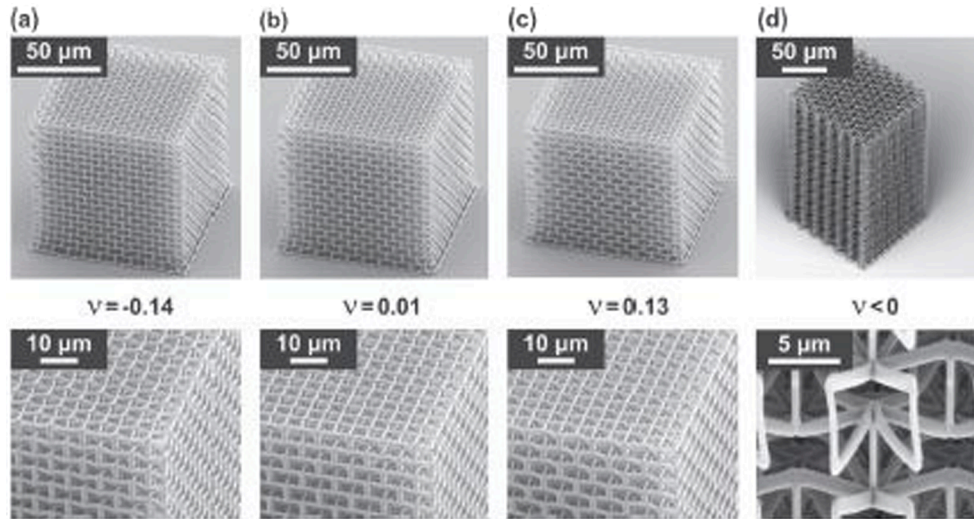


Fig. 32. (a)–(c) trilinear structures with the four-fold axis of rotation. (d) trilinear structure with a six-fold axis of rotation. Lower row images are magnified images of the respective images on the top row. From [125].

of the indentation was effectively seen when the surface was exposed to light with a wavelength in the range of 500–900 nm as illustrated in Fig. 35 (c).

In 2013, Buckmann and his group [131] ventured into mechanical cloaking utilizing pentamode metamaterials via their novel “dip-in” 3D DLW technique. Experimental demonstration of a core-shell-based elasto-mechanical cloak was achieved. As shown in Fig. 36, the structure consisted of three crucial components. First, the rigid core-shell wall protects any object placed inside it. Second and third being the homogeneous, isotropic surroundings with high FOM to make the core-shell geometry appear elastically as its surroundings. Intuitively, the system

can be compared to a spring-mass mechanical system with three different spring constants: one is very stiff and the other two are made softer to compensate for the effect exhibited by the stiff spring and finally, the effective spring constant is the same as that of system with three identical springs. The structure had a macroscopic volume of 2 mm^3 with 1024 face-centered cubic unit cells and a lattice constant of $125 \mu\text{m}$. Three structures were fabricated: 1) without the core-shell rigid wall acting as the reference, 2) Core-shell wall with a homogeneous isotropic surrounding of B/G ratio ~ 120 , and 3) cloaking structure consisting of the core-shell, homogeneous and isotropic surroundings with two regions of B/G ~ 908 near the core-shell wall and B/G ~ 120

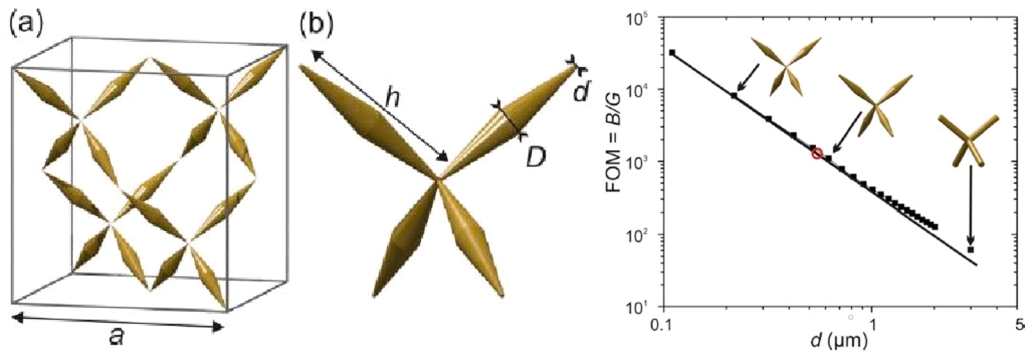


Fig. 33. (a) Depiction of pentamode metamaterial suggested by Milton and Cherkaev. (b) Illustration of the approximated pentamode ideal with a finite diameter, d in the connecting regions of the touching cones. (Right) Dependence of FOM with the diameter, d . From [126].

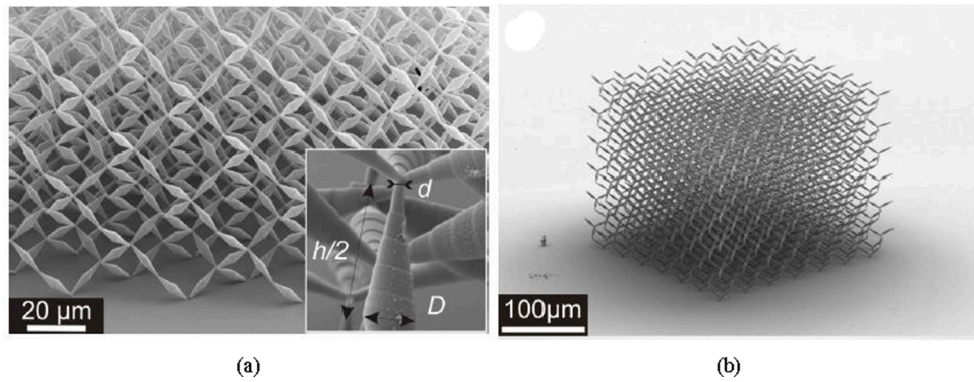


Fig. 34. (a) Electron micrograph of a polymer pentamode mechanical metamaterial fabricated by “dip-in” 3D DLW with $h = 16.15 \mu\text{m}$, $D = 3 \mu\text{m}$ and $d = 0.55 \mu\text{m}$. (b) another pentamode metamaterial with $h = 16.15 \mu\text{m}$, $D = 3 \mu\text{m}$ and $d = 1 \mu\text{m}$. From [126].

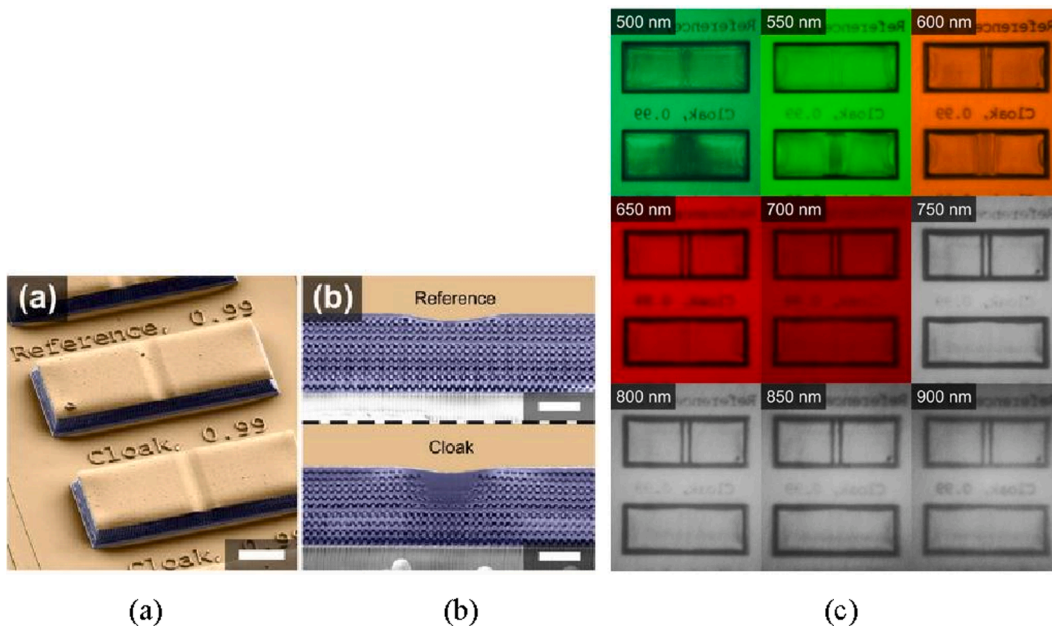


Fig. 35. a) Electron micrograph of (top) polymer reference and (bottom) cloaking structures. (b) Corresponding FIB cuts of the structures. (Right) Optical micrographs of illumination wavelengths ranging from 500 to 900 nm. From [130]. The length scale is 10 μm .

away from the wall. Finally, these structures were subjected to compression loading from the top using a hard silicon stamp and the results obtained successfully displayed elastic “unfeelability” as shown in the plots in Fig. 37. Detailed reviews on optical, mechanical, and acoustic metamaterials fabricated using several techniques can be found

in ref. [132–135].

7. Conclusions and future direction

This review introduces the reader to the true three-dimensional

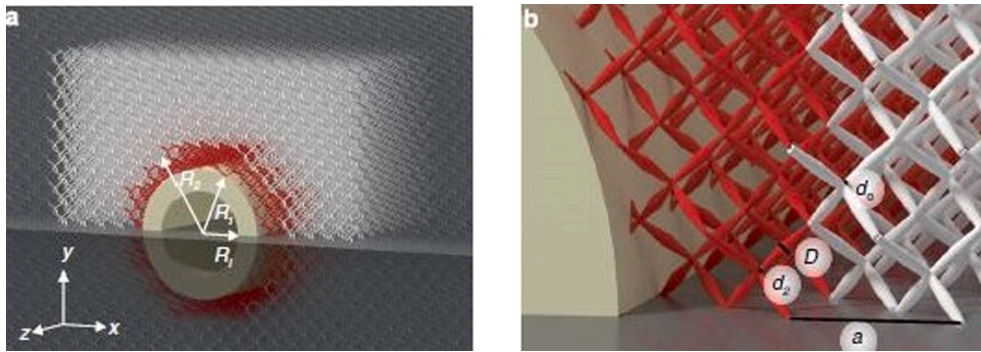


Fig. 36. a) Pentamode mechanical metamaterial with a rigid core-shell element surrounded by a flexible homogeneous, isotropic polymer material. b) magnified view of the near surroundings of the core-shell element. From [131].

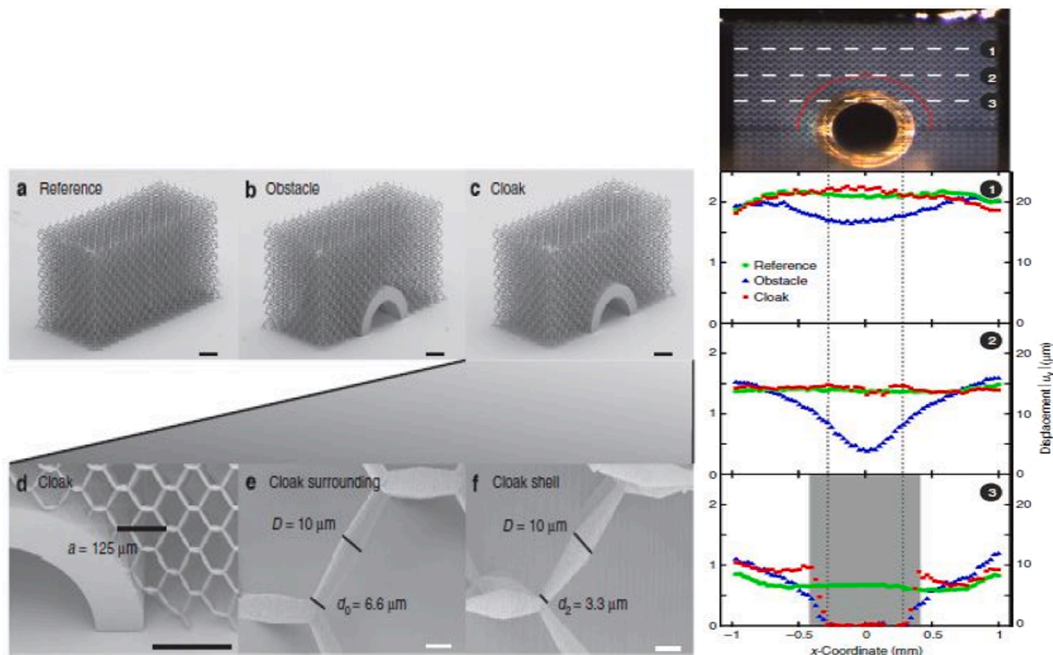


Fig. 37. (left) a) Reference structure without the core-shell element. b) Reference structure with the rigid hollow semi-cylinder (obstacle). c) Cloaking structure with core-shell element and varying surroundings as specified. (d-f) magnified view of (c) with dimensions farther and near surroundings respectively. (Right) Optical photograph of the cloaking structure when subjected to compression loading from the top. As shown the strain is similar for both the reference and cloaking structures. From [131].

fabrication of microstructures using femtosecond lasers based on the nonlinear optical process called two-photon lithography (TPL). TPL is highly capable of fabricating nanoscale features and has proven to be an imperative technique for the 3D microfabrication of numerous materials for a myriad of applications, viz. tissue engineering, 3D scaffolding, drug delivery, biomimetics, microelectronics and metamaterials. As discussed, improved resolution and scalability can be achieved by incorporating certain technologies with TPL such as the usage of spatial light modulators (SLMs), digital micromirror devices (DMDs), and microlens arrays (MLAs) and can pave a way for industrialization which until now has been confined only to research laboratories. Further in the future, based on demand, TPL can be extended beyond microscale into the centimeter regime by integrating various additive and subtractive techniques. Furthermore, TPL is the only technique that caters to the need for high dimensional accuracy and true 3D fabrication, which can play a crucial role in the future development of metamaterials for data storage, waveguides and terahertz applications. TPL can also play a vital role in the fabrication of functional, nonstructural materials viz. electronic materials, energy storage materials. Another region of interest for

researchers is multi-material fabrication in the nanoscale regime. Incorporating several materials with different mechanical, optical, and electrical properties in a single nanostructure is a huge challenge and currently there is no evidence of multi-material fabrication via TPL. However, with recent advancements, TPL has great potential for tailoring the composition and structure simultaneously at the nanoscale which can prove to be revolutionary in the field of photonics, electromagnetic metamaterials, mechanical metamaterials, and biomaterials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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